Electronic Supplementary Information

Bi(III)-Catalyzed Aminooxygenation of Propargyl Amidines to Synthesize 2-Fluoroalkyl Imidazole-5-Carbaldehydes and Their Decarbonylations

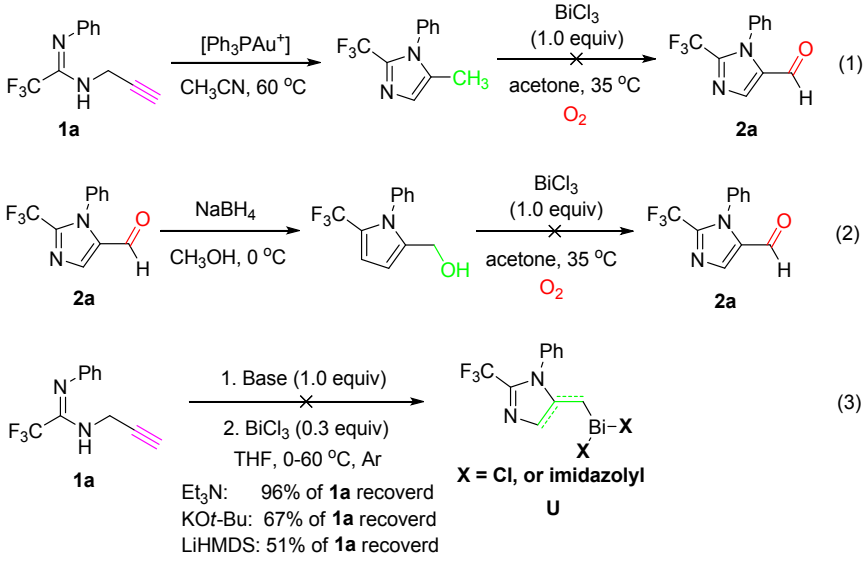
Table of content

I. General Information

Melting points were measured on a Melt-Temp apparatus and were uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM-400 spectrometer (400 MHz) with TMS as internal standard. ^{19}F NMR spectra were taken on a Bruker AM-400 (282 MHz) spectrometer using $CFCl_3$ as external standard. ^{13}C NMR spectra were taken a Bruker AM-400 (101 MHz) spectrometer. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Mass spectra were recorded in Zhejiang University and elemental analyses were recorded in Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Solvents were purchased form commercial sources and purified before used by standard procedures. Unless otherwise specified, all reactions were carried out in a Schlenk tube and magnetic stirring under an ambient circumstance. TLC analysis was performed on silica gel plates, column chromatography over silica gel (mesh 300-400) and petroleum ether-ethyl acetate combination was used as the eluent.

II. Preliminary Mechanistic Studies on $BiCl_3$-Catalyzed Aminooxygenation

Scheme S1. Investigation on reaction intermediates



Upon exposure of 5-methyl imidazole and 5-hydroxymethyl imidazole, possible intermediates in this transformation, no **2a** was formed even with 1.0 equiv of $BiCl_3$.

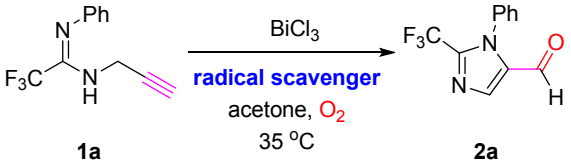
The formation of **U** under basic conditions[1] was not detected, which indicated that the construction of C-Bi(III) bond directly in this reaction was impossible.

Reference

[1] (a) H. H. Peng, N. G. Akhmedov, Y. F. Liang, N. Jiao and X. D. Shi, *J. Am. Chem. Soc.* 2015, **137**, 8912; (b) S. Li, Z. K. Li, Y. F. Yuan, D. J. Peng, Y. J. Li, L. S. Zhang, and Y. M. Wu, *Org. Lett.* 2012, **14**, 1130; (c) A. N. Dunlop, R. J. Kominar and S. J. W. Price, *Can. J. Chem.* 1970, **48**, 1269.

Scheme S2. Investigation on reaction pathway

(A) Effect of radical scavengers on aminooxygenation

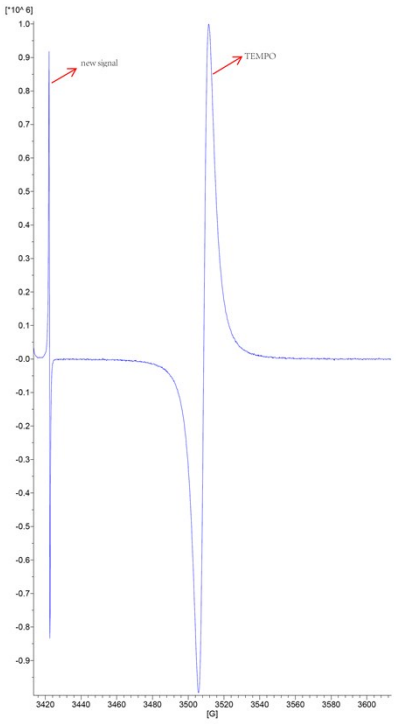


1a **2a**

$BiCl_3$	radical scavenger	phenol	**2a**
-	TEMPO (3.0 equiv)	-	-[a]
0.05 equiv	- (-)	-	44%
1.0 equiv	TEMPO (3.0 equiv)	-	76%
0.3 equiv	TEMPO (1.0 equiv)	-	28%
0.05 equiv	TEMPO (0.15 equiv)	-	9%
0.05 equiv	TEMPO (0.15 equiv)	0.15 equiv	/[b]
0.05 equiv	BHT (0.15 equiv)	-	23%
0.05 equiv	BHT (0.15 equiv)	0.15 equiv	51%

[a] no reaction. [b] no desired product

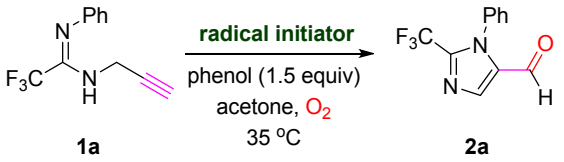
(**B**) EPR for $BiCl_3$-catalyzed aminooxygenation



Without phenol, the addition of TEMPO dramatically decreased the efficiency of aminooxygenation; however, no TEMPO-R adduct was detected by GC-MS and LC-MS analysis. When phenol and TEMPO were added simultaneously, the reaction became messy. Similar results were detected In the presence of BHT. Based on these results, it was considered that radicals were involved in the reaction, which was supported by EPR analysis.

Scheme S3. Investigation on reaction initial step

(A) Effect of radical initiator on aminooxygenation

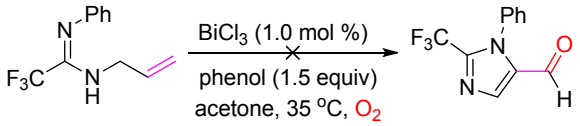


1a **2a**

radical initiator (0.10 equiv)	$BiCl_3$	time	**2a**
-[a]	0.05 equiv	6 h	92%
DTBP	-	16 h	-[b]
DTBP	0.05 equiv	9 h	80%
BPO	-	16 h	-
BPO	0.05 equiv	7 h	73%
AIBN	-	16 h	-
AIBN	0.05 equiv	7 h	71%

[a] no addtion. [b] no reaction.

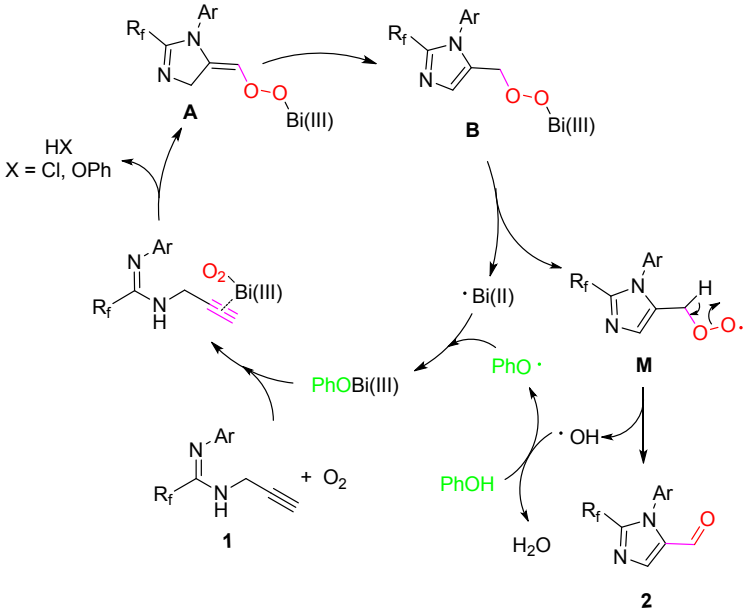
(B) Investigation on aminooxygenation of alkene



1a' **2a**

The addition of radical initiators into the model reaction did not facilitate this transformation, Without $BiCl_3$, no reaction occurred with 10 mol% of radical initiators, such as DTBP, BPO, and AIBN. Addition of these radical initiators to the model reaction resulted in longer time and decreased yields. In addition, no reaction occurred when allyl amidine **1a'** was used under the standard reaction conditions. Those results suggested that the reaction might be initiated by an alternative pathway rather than a radical pathway.

Scheme S4. Proposed mechanism of Bi(III)-catalyzed aminooxygenation



Although a detailed reaction pathway still remains to be clarified, a proposed mechanism is shown in Scheme S4. Coordination of the triple bonds of substrate **1** and dioxygen[1] with Bi(III) generates a Bi-peroxy intermediate **A** by a three-component intermolecular nucleophilic substitution. Then, **A** isomerizes to a more stable species **B** via H-1,3-shift. The Bi-O_2 bond in **B** dissociates into a ·Bi(II) species and a peroxyl radical **M**. Desired product **2** forms from **M** by means of removal of a hydroxyl radical[2] that would convert to H_2O in the presence of phenol[3]. PhOBi(III) species, generated from the combination of the ·Bi(II) species and the PhO· radical, keeps the reaction going on.

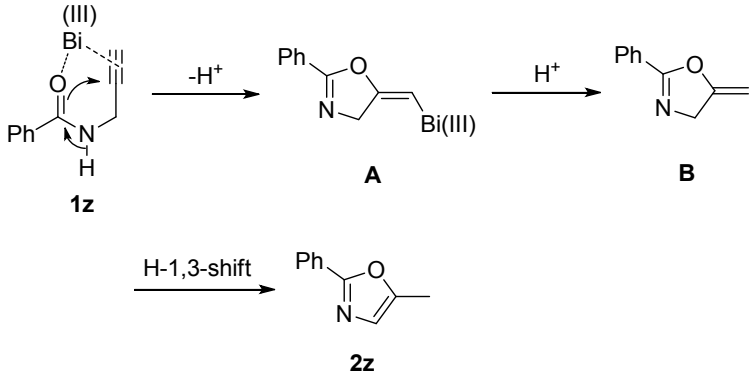
Reference

1 (a) Y. J. Pang, X. H. Chen, C. Z. Xu, Y. J. Lei and K. M.Wei, *ChemCatChem* 2014, **6**, 876; (b) B. G. M. Rocha, M. L. Kuznetsov, Y. N. Kozlov, A. J. L. Pombeiro and G. B. Shul' pin, *Catal. Sci. Technol.* 2015, **5**, 2174; (c) M. L. Kuznetsov, B. G. M. Rocha, A. J. L. Pombeiro and B. G. Shul' pin, *ACS Catal.* 2015, **5**, 3823.

2 (a) H. H. Peng, N. G. Akhmedov, Y. F. Liang, N. Jiao and X. D. Shi, *J. Am. Chem. Soc.* 2015, **137**, 8912; (b) S. Li, Z. K. Li, Y. F. Yuan, D. J. Peng, Y. J. Li, L. S. Zhang, and Y. M. Wu, *Org. Lett.* 2012, **14**, 1130; (c) S. Li, Z. K. Li, Y. F. Yuan, D. J. Peng, Y. J. Li, L. S. Zhang, and Y. M. Wu, *Chem. Eur. J.* 2013, **19**, 1496.

3 M. J. Lundqvist and L. A. Eriksson, *J. Phys. Chem. B* 2000, **104**, 848; (b) N. Agnihotri and P. C. Mishra, *J. Phys. Chem. A* 2011, **115**, 14221; (c) C. Cren-Olivé, P. Hapiot,; J. Pinson and C. Rolando, *J. Am. Chem. Soc.* 2002, **124**, 14027; (d) D. Zhang, Y. X. Liu, L. Chu, Y. Wei, D. Wang, S. B. Cai, F. Zhou and B. P Ji,. *J. Phys. Chem. A* 2013, **117**, 1784; (e) D. D. Li, R. M. Han, R. Liang, C. H. Chen, W. Z. Lai, J. P. Zhang and L. H. Skibsted, *J. Phys. Chem. B* 2012, **116,** 7154.

Scheme S5. Possible mechanism of the formation of 2z



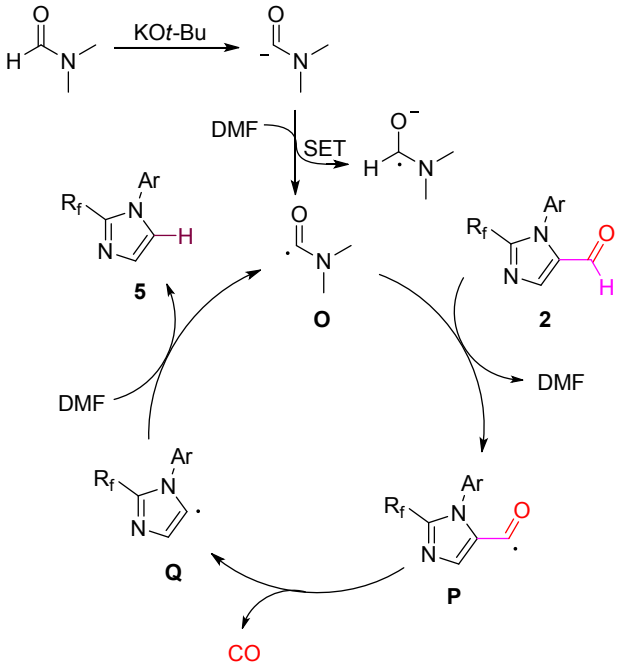
A possible mechanism of the formation of **2z** was proposed, as described in scheme S5, both C-C triple bonds and the amide group are activated by coordination with the Bi-catalyst. Then, the C-C triple bonds accept the attack of oxygen atom on amide to afford intermediate **A**[1] which undergoes protodemetallation to give an intermediate **B**. The final product **2z** forms form **B** via an H-1,3-shift.

Reference

1 (a) M. Y. Chang, Y. C. Cheng and Y. J. Lu, Org. Lett. 2015, **17**, 1264; (b) K. Komeyama, M. Miyagi and K. Takaki, Heteroat. Chem. 2008, **19**, 644; (c) K. Komeyama, K. Takahashi and K. Takaki, Org. Lett. 2008, **10**, 5119.

III. Scheme S6. Possible Mechanism of KO*t*-Bu-Mediated Decarbonylation

Scheme S6. Possible mechanism of KO*t*-Bu-mediated decarbonylation



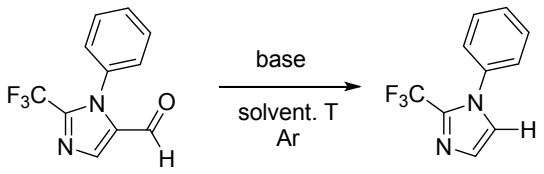
Based on the previous work, a possible mechanism of KO*t*-Bu-mediated decarbonylation was proposed and described in Scheme S6, DMF is deprotonated by KO*t*-Bu to afford the carbonyl anion which undergoes a single-electron transfer step (**SET**) to generate the carbamoyl radical **O**. Then, the carbamoyl radical **O**[1] abstracts a hydrogen atom to give an imidazolyl-5-acyl radical **P**. Imidazolyl radical Q, formed from **P** by releasing a molecule of CO, converts to the desired product **5** by capturing a hydrogen atom on DMF.

Reference

1 (a) C. B. de Koning, J. P. Michael and A. L. Rousseau, J. Chem. Soc. Perkin Trans. 1. 2000, 787; (b) R. Pathak, K. Vandayar, W. A. L. van Otterlo, J. P. Michael, M. A. Fernandes and C. B. de Koning, Org. Biomol. Chem. 2004, **2**, 3504; (c) Y. Y. Chen, X. J. Zhang, H. M. Yuan, W. T. Wei and M. Yan, Chem. Commun. 2013, **49**, 10974; (d) W. T. Wei, X. J. Dong, S. Z. Nie, Y. Y. Chen, X. J. Zhang and M. Yan, Org. Lett. 2013, **15**, 6018; (e) W. J. Wang, X. Zhao, L. Tong, J. H. Chen, X. J. Zhang and M. Yan, J. Org. Chem. 2014, **79**, 8557; (f) W. T. Wei, Y. Liu, L. M. Ye, R, H. Lei, X. J. Zhang and M. Yan, Org. Biomol. Chem., 2015, **13**, 817; (g) Y. Y. Chen, N. N. Zhang, L. M. Ye, J. H. Chen, X. Sun, X. J. Zhang and M. Yan, RSC adv. 2015, 59, 48046.

IV. Table S1. Optimized for the Base-Mediated Decarbonylation

Table S1. Optimized for the base-mediated decarbonylation[a]



2a **5a**

Entry	Base	Amt	Solvent	T	Yield[b]
1	KO*t*-Bu	1.2 equiv	DMF	80 ℃	32%[c]
2	KO*t*-Bu	2.0 equiv	DMF	80 ℃	65%
3	KO*t*-Bu	3.0 equiv	DMF	80 ℃	76%
4	K_2CO_3	3.0 equiv	DMF	80 ℃	-[d]
5	Cs_2CO_3	3.0 equiv	DMF	80 ℃	-
6	K_3PO_4	3.0 equiv	DMF	80 ℃	-
7	KOH	3.0 equiv	DMF	80 ℃	43%
8	Et_3N	3.0 equiv	DMF	80 ℃	-
9	KO*t*-Bu	3.0 equiv	DMF	60 ℃	79%
10	**KO*t*-Bu**	**3.0 equiv**	**DMF**	**45 ℃**	**84%**
11	KO*t*-Bu	3.0 equiv	DMF	35 ℃	61%
12	KO*t*-Bu	3.0 equiv	toluene	45 ℃	56%
13	KO*t*-Bu	3.0 equiv	dioxane	45 ℃	77%
14	KO*t*-Bu	3.0 equiv	CH_3CN	45 ℃	-
15	KO*t*-Bu	3.0 equiv	DMSO	45 ℃	22%
16	KO*t*-Bu	3.0 equiv	*t*-BuOH	45 ℃	/[e]
17	KO*t*-Bu	3.0 equiv	DMF	45 ℃	71%[f]

[a] Reaction conditions: **2a** (1.0 mmol), solvent (5.0 mL), Ar. [b] Isolated yield. [c] With 43% starting material recovered. [d] "-" no reaction. [e] "/" no desired product. [f] react in air。

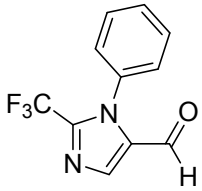
V. General Procedure for the Synthesis of Imidazole-5-Carbaldehyde

Under oxygen atmosphere, to a Schlenk tube with a stirring bar was added $BiCl_3$

(1.6 mg, 1.0 mol %), 2-fluoroalkyl propargyl amidine (0.5 mmol), phenol (71 mg, 1.5 equiv) and acetone (6.0 mL). The system was then heated to 35 ℃ and monitored by TLC. The solvent was removed under vacuum when the reaction came to the end. The crude product was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (7:1) as the eluent to give the desired product.

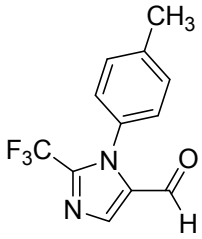
VI. Characterization for the 2-Fluoroalkyl Imidazole-5-Carbaldehyde

1-Phenyl-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (2a)



White solid, m. p.: 60 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 7.93 (s, 1H), 7.56 (m, 3H), 7.37 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -60.14 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.7, 140.7 (q, J = 38.6 MHz), 137.7, 134.7, 133.6, 130.6, 129.5, 127.2, 117.7 (q, J = 270.5 MHz). MS (EI), m/e (%): 240 (M^+, 26), 78 (100). IR (film): ν 1683, 1530, 1500, 1456, 1358, 1198, 1150, 819 cm^{-1}. Anal. Calcd. for $C_{11}H_7F_3N_2O$: C, 55.01; H, 2.94; N, 11.66; Found: C, 54.77; H, 11.84; N, 2.83.

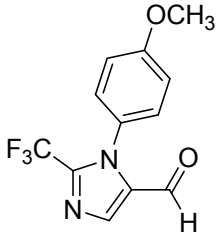
1-(*p*-tolyl)-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (2b)



White solid: m. p.: 74-76 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.92 (s, 1H), 7.34 (d, J = 8.0 MHz, 2H), 7.24 (d, J = 8.0 MHz, 2H), 2.47 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.56 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 141.0, 140.7 (q, J = 26.3 MHz), 137.5, 134.8, 130.9, 130.2, 126.9, 180.1 (q, J = 270.0 MHz). HRMS (EI), Calcd. for $C_{12}H_9F_3N_2O$: 254.0667; Found: 254.0668. IR (film) ν 2845, 1684, 1542, 1477, 1344, 1172, 1113, 985, 866 cm^{-1}.

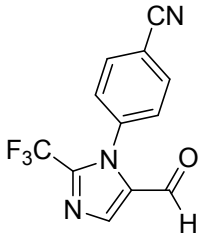
1-(4-Methoxyphenyl)-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (2c)

White solid, m. p.: 116-117 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 7.91 (s, 1H), 7.28 (d, J = 12.0 MHz, 2H), 7.02 (d, J = 12.0 MHz, 2H), 3.89 (s, 3H). ^{19}F NMR (282 Hz, $CDCl_3$): δ -60.99 (s). ^{13}C NMR (101 MHz, $CDCl_3$): δ 179.0, 161.0, 140.9 (q, J = 39.1 MHz), 137.4, 134.9, 128.3, 125.9, 118.2 (q, J = 266.1 MHz), 114.6, 55.6.



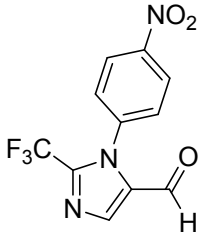
HRMS (EI), Calcd. for $C_{12}H_9N_2O_2F_3$: 270.0616; Found: 270.0613. IR (film): ν 1720, 1599, 1558, 1502, 1448, 1373, 1304, 1190, 1132, 968, 788, 695 cm^{-1}.

4-(5-Formyl-2-(trifluoromethyl)-1H-imidazol-1-yl)benzonitrile (2d)



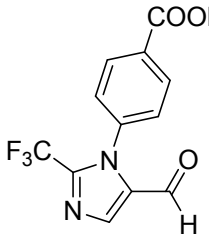
White solid, m. p.: 106-108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.78 (d, *J* = 8.0 MHz, 2H), 7.41 (d, *J* = 8.0 MHz, 2H). ^{19}F (282 MHz, $CDCl_3$) δ -60.20 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.35, 140.01 (q, *J* = 39.4 MHz), 139.80, 137.81, 133.72, 133.34, 128.16, 118.83 (q, *J* = 273.7 MHz), 117.34, 114.79. HRMS (EI), Calcd. for $C_{12}H_6F_3N_3O$: 265.0463; Found: 265.0464. IR (film): ν 2234, 1692, 1644, 1508, 1452, 1283, 1188, 1142, 855 cm^{-1}.

1-(4-Nitrophenyl)-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (2e)



White solid, m. p.: 151-154 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.33 (d, *J* = 8.0 MHz, 2H), 7.90 (s, 1H), 7.47 (d, *J* = 8.0 MHz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.17 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.38, 148.76, 141.03 (q, *J* = 39.4 MHz), 139.94, 139.33, 132.4, 128.40, 124.78, 117.93 (q, *J* = 292.9 MHz). HRMS (EI), Calcd. for $C_{11}H_6F_3N_3O_3$: 285.0361; Found 285.0362. IR (film): ν 1697, 1643, 1635, 1587, 1530 (d), 1495 (d), 1452, 1348, 1292, 1188, 1148 (d), 861 (d) cm^{-1}.

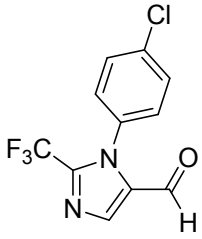
ethyl 4-(5-formyl-2-(trifluoromethyl)-1H-imidazol-1-yl)benzoate (2f)



White solid, m. p.: 93-95 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 8.23 (d, *J* = 8.4 MHz, 2H), 7.95 (s, 1H), 7.43 (d, *J* = 8.4 MHz, 2H), 4.44 (q, *J* = 7.2 MHz, 2H), 1.43 (t, *J* = 7.2 MHz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -59.97 (s). ^{13}C NMR (101 MHz, CDCl3): δ 178.4, 165.1, 140.9 (q, *J* = 39.3 MHz), 138.8, 137.5, 134.5, 132.7, 130.7, 127.2, 117.5, 269.7 (q, *J* = 269.7 MHz), 61.6, 14.3. MS (EI), m/e (%): 312 (M^+, 33), 105 (100), 267 (81). IR (film): ν1717, 1693, 1532, 1452, 1354, 1278, 1186, 1137 cm-

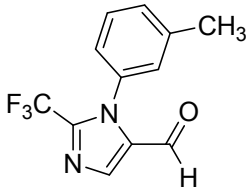
1. Anal. Calcd. for $C_{14}H_{11}F_3N_2O_3$:C, 53.85; H, 3.55; N, 8.97; Found: C, 54.04; H, 3.65; N, 8.88.

1-(4-Chlorophenyl)-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (2g)



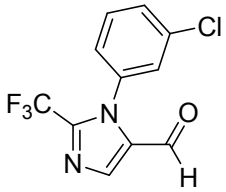
White solid, m. p.: 84 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (s, 1H), 7.93 (s, 1H), 7.53 (d, *J* = 8.7 MHz, 2H), 7.31 (d, *J* = 8.7 MHz, 2H). ^{19}F NMR (282 Hz, $CDCl_3$): δ -60.03 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 141.0 (q, *J* = 38.7 MHz), 138.7, 136.8, 134.5, 132.3, 129.8, 128.4, 117.5 (q, *J* = 270.5 MHz). MS (EI), m/e (%): 274 (M^+, 27), 112 (100). IR (film): ν 1693, 1532, 1497, 1353, 1185, 1137, 841 cm^{-1}. Anal. Calcd. for $C_{11}H_6F_3N_2ClO$: C, 48.11; H, 2.20; N. 10.20; Found: C, 48.00; H, 2.26; N, 10.08.

1-*m*-Tolyl-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (2h)



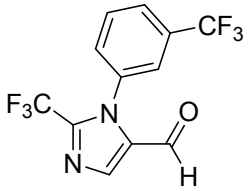
White solid, m. p.: 29-33 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.53 (s, 1H), 7.85 (s, 1H), 7.34 (m, 2H), 7.10 (s, 2H), 2.02 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -60.20 (s). ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.9, 140.6 (q, *J* = 39.0 MHz), 139.9, 137.2, 134.8, 133.4, 131.4, 129.3, 127.6, 124.2, 117.5 (q, *J* = 269.7 MHz), 21.2. MS (EI), m/e (%): 254 (M^+, 35), 92 (100). IR (film): ν 1693, 1530, 1497, 1363, 1211, 1175, 1140, 817 cm^{-1}. Anal. Calcd. for $C_{12}H_9F_3N_2O$: C, 56.70; H, 3.57; N, 11.02; Found: C, 56.57; H, 5.54; N, 11.20.

1-(3-chlorophenyl)-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (2i)



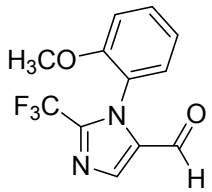
White solid, m. p.: 51-54 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.85 (s, 1H), 7.51 (m, 1H), 7.41 (m, 1H), 7.30 (s, 1H), 7.19 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.36 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 140.8 (q, *J* = 39.4 MHz), 138.6, 135.2, 134.7, 134.5, 130.9, 130.4, 127.4, 125.5, 117.8 (q, *J* = 272.7 MHz). HRMS (EI), Calcd. for $C_{11}H_6F_3ClN_2O$: 274.0121; Found: 274.0122. IR (film) ν 1712, 1659, 1595, 1514, 1350, 1252, 1196, 1142, 1042, 1028, 896, 721 cm^{-1}.

2-(trifluoromethyl)-1-(3-(trifluoromethyl)phenyl)-1H-imidazole-5-carbaldehyde (2j)



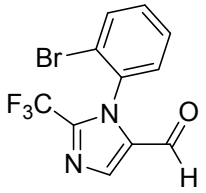
White solid, m. p.: 74-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.87 (s, 1H), 7.77 (m, 1H), 7.62 (m, 1H), 7.54 (m, 1H), 7.48 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.34 (s), -62.86 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.39, 141.10 (q, J = 39.4 MHz), 139.21, 134.48, 132.15 (q, J = 33.3 MHz), 130.51, 130.19, 127.42 (q, J = 3.0 MHz), 124.25 (q, J = 4.0 MHz), 123.07 (q, J = 273.7 MHz), 122.10, 117.81 (q, J = 268.7 MHz). HRMS (EI), Calcd. for $C_{12}H_6F_6N_2O$: 308.0384; Found: 308.0385. IR (film): ν 1695, 1535, 1499, 1460, 1333, 1271, 1184, 1130 (d), 1041, 820, 698 cm^{-1}. Anal. Calcd. for $C_{12}H_6F_6N_2O$: C,46.77; H, 1.96; N, 9.09; Found: C, 46.89; H, 2.01; N, 9.18.

1-(2-Methoxyphenyl)-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (2k)



White solid: m. p.: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.84 (s, 1H), 7.46 (m, 1H), 7.23 (d, J = 8.0 MHz, 1H), 7.01 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.83 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.99, 154.70, 140.64 (q, J = 39.4 MHz), 137.45, 134.45, 132.07, 128.34, 122.45, 120.667, 118.03 (q, J = 272.7 MHz), 111.92, 55.84. HRMS (EI), Calcd. for $C_{12}H_9F_3N_2O_2$: 270.0616; Found: 270.0617. IR (film): ν 1693, 1533, 1508, 1467, 1282, 1188, 1140, 1049, 1024, 968, 816, 754 (d) cm^{-1}.

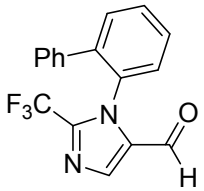
1-(2-iodophenyl)-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (2l)



White solid: m. p.: 44-46 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62, 7.87, 7.67 (d, J = 8.0 MHz, 1H), 7.38 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.54 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 140.4 (q, J = 39.4 MHz), 138.7, 134.0, 133.6, 133.6, 132.0, 128.8, 128.4, 122.0, 117.9 (q, J = 290.9 MHz). HRMS (EI), Calcd. for $C_{11}H_6BrF_3N_2O$: 317.9616/319.9595; Found: 317.9617/319.9596. IR (film): ν 1692, 1534, 1496, 1474,

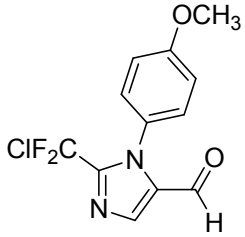
1354, 1187, 1143, 815 cm^{-1}.

1-([1,1'-biphenyl]-2-yl)-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (2m)



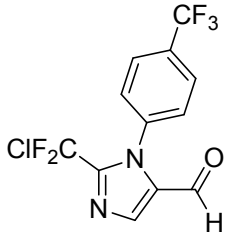
White solid, m. p.: 91-93 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.44 (s, 1H), 7.66 (m, 2H), 7.54 (t, *J* = 7.1 MHz, 1H), 7.42 (d, *J* = 8.1 MHz, 1H), 7.24 (m, 3H), 7.03 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -59.85 (s). ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.6, 140.7 (q, *J* = 38.6 MHz), 140.0, 137.9, 137.0, 134.5, 131.7, 131.3, 130.9, 128.5, 128.4, 128.2, 128.0, 127.6, 117.5 (q, *J* = 270.5 MHz). MS (EI), m/e (%): 316 (M^+, 64), 247 (100), 154 (71), 287 (42). IR (film): ν 1692, 1531, 1490, 1444, 1352, 1185, 1143, 817 cm^{-1}. Anal. Calcd. for $C_{17}H_{11}F_3N_2O$: C,64.56; H, 3.51; N, 8.86; Found: C, 64.47; H, 3.58; N, 8.80.

2-(Chlorodifluoromethyl)-1-(4-methoxyphenyl)-1H-imidazole-5-carbaldehyde (2n)



White solid, m. p.: 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51, 7.82, 7.21 (d, *J* = 8.0 MHz, 2H), 6.94 (d, *J* = 8.0 MHz, 2H), 3.81 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -48.02 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.09, 160.84, 144.27 (t, *J* = 31.8 MHz), 137.17, 134.97, 128.66, 126.09, 119.87 (t, *J* = 289.9 MHz), 114.52, 55.60. HRMS (EI), Calcd. for $C_{12}H_9ClF_2N_2O_2$: 286.0321; Found: 286.0320. IR (film): ν 1690, 1608, 1514, 1452, 1350, 1302, 1253, 1172, 1150, 1110, 1032 (d), 989, 903, 839, 768 cm^{-1}.

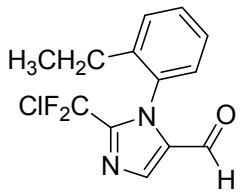
2-(chlorodifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-1H-imidazole-5-carbaldehyde (2o)



White solid, m. p. 122-124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.87 (s, 1H), 7.74 (d, *J* = 8.0 MHz, 2H), 7.43 (d, *J* = 8.0 MHz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -47.90 (s, 2F), -62.81 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 143.5 (t, *J* = 32.8 MHz), 138.1, 136.3, 133.4, 131.6 (q, *J* = 33.3 MHz), 127.1, 125.6, 122.33 (q, *J* = 273.7 MHz), 118.7 (t, *J* = 289.9 MHz). HRMS (EI), Calcd. for $C_{12}H_6ClF_5N_2O$:

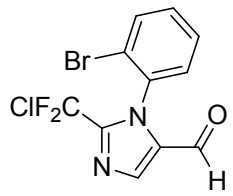
324.0089; Found: 324.0091.IR (film) ν 1692, 1529, 1447, 1323, 1217, 1132, 1107, 993, 900, 852 cm^{-1}. Anal. Calcd. for $C_{12}H_6ClF_5N_2O$: C,44.40; H, 1.86; N, 8.83; Found: C, 44.53; H, 1.90; N, 8.74.

2-(chlorodifluoromethyl)-1-(2-ethylphenyl)-1H-imidazole-5-carbaldehyde (2p)



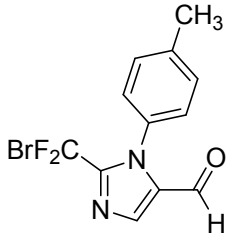
White solid, m. p.: 77-78 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.88 (s, 1H), 7.47 (m, 1H), 7.39 (m, 1H), 7.28 (m, 1H), 7.19 (m, 1H), 2.19 (m, 2H), 1.06 (t, *J* = 8.0 MHz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 48.87 (d, *J* = 16.9 MHz). ^{13}C NMR (400 MHz, $CDCl_3$) δ 178.9, 144.0 (t, *J* = 32.3 MHz), 141.1, 137.7, 134.5, 132.5, 130.9, 127.6, 126.7, 119.9 (t, *J* = 299.0 MHz), 23.2, 13.5. HRMS (EI), Calcd. for $C_{13}H_{11}ClF_2N_2O$: 284.0528; Found: 284.0524. IR (film) ν 1691, 1530, 1492, 1454, 1348, 1171, 109, 993, 903 cm^{-1}.

1-(2-bromophenyl)-2-(chlorodifluoromethyl)-1H-imidazole-5-carbaldehyde (2q)



Light yellow solid. m. p.: 63-64 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.86 (s, 1H), 7.67 (m, 1H), 7.40 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -49.18 (q). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 143.8 (t, *J* = 32.3 MHz), 138.5, 133.9, 133.8, 133.5, 131.9, 129.2, 128.3, 122.3, 119.7 (t, *J* = 289.9 MHz). HRMS (EI), Calcd. for $C_{11}H_6ClBrF_2N_2O$:298.9632 (M-Cl); Found: 298.9628 (M-Cl).IR (film) ν 1962, 1531, 1485, 1348, 1170, 1111, 991, 895, 756 cm^{-1}.

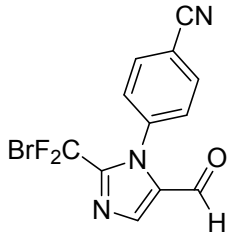
2-(Bromodifluoromethyl)-1-p-tolyl-1H-imidazole-5-carbaldehyde (2r)



White solid. ^1H NMR (300 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.90 (s, 1H), 7.35 (d, *J* = 8.4 MHz, 2H), 7.27 (d, *J* = 8.4 MHz, 2H), 2.47 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -44.97 (s). ^{13}C NMR (101 MHz, $CDCl_3$): δ 188.0, 144.9 (t, *J* = 29.1 MHz), 140.8, 137.3, 134.7, 131.2, 130.0, 127.2, 111.2 (t, *J* = 300.4 MHz), 21.3. HRMS (EI), Calcd. for $C_{12}H_9N_2OF_2Br$: 313.9866; Found: 313.9861. IR (film): ν 2850, 1690, 1531, 1484,

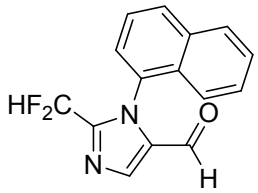
1348, 1172, 1111, 984, 861 cm^{-1}.

4-(2-(bromodifluoromethyl)-5-formyl-1H-imidazol-1-yl)benzonitrile (2s)



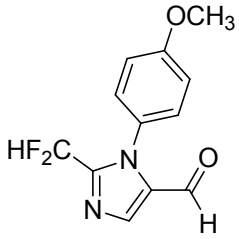
White solid, m. p.: 106-107 ℃. ^1H NMR (300 MHz, $CDCl_3$): δ 9.76 (s, 1H), 7.97 (s, 1H), 7.87 (d, J = 8.4 MHz, 2H), 7.52 (d, J = 8.4 MHz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -44.49 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.4, 145.3 (t, J = 29.5 MHz), 139.7, 138.3, 134.2, 133.2, 128.6, 117.4, 114.7, 110.2 (t, J = 300.8 MHz). MS (EI), m/e (%): 325 (M^+, 1.6), 246 (100). IR (film): ν 2851, 2232, 1681, 1528, 1507, 1442, 1342, 1170, 1105, 991, 866, 570 cm^{-1}. Anal. Calcd. for $C_{12}H_6BrF_2N_3O$: C, 44.20; H, 1.85; N, 12.89; Found: C, 44.11; H, 1.81; N,13.11.

2-(difluoromethyl)-1-(naphthalen-1-yl)-1H-imidazole-5-carbaldehyde (2t)



White solid, m. p.: 185-188 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.98 (m, 2H), 7.90 (m, 1H), 7.49 (m, 4H), 7.03 (m, 1H), 6.41 (t, J = 12.0 MHz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.81 (qd, J_1 = 39.5 MHz, J_2 = 67.7 MHz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 144.4 (q, J = 27.3 MHz), 137.3, 133.8, 132.9, 130.0, 129.0, 127.5, 127.3, 126.3, 124.8, 124.0, 120.1, 107.1 (t, J = 239.4 MHz). HRMS (EI), Calcd. for $C_{15}H_{10}F_2N_2O$: 272.0761; Found: 272.0759. IR (film) ν 1682, 1531, 1468, 1454, 1402, 1369, 1169, 1117, 1047, 820, 772 cm^{-1}.

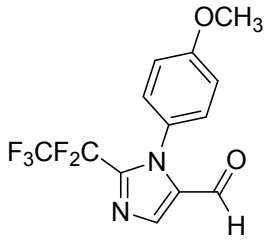
2-(Difluoromethyl)-1-(4-methoxyphenyl)-1H-imidazole-5-carbaldehyde (2u)



White Solid，m. p.: 139-142 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.57, 7.83, 7.22 (d, J =12.0 MHz, 2H), 6.94 (d, J = 12.0 MHz, 2H), 6.51 (t, J = 52.0 MHz, 1H), 3.81 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.86 (d, J = 52.64 MHz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.02, 160.72, 144.93 (t, J = 21.0 MHz), 138.53, 134.33, 128.36, 126.02, 114.62, 108.41 (t, J = 238.0 MHz), 55.60. HRMS (EI), Calcd. for $C_{12}H_{10}F_2N_2O_2$: 252.0710; Found: 252.0709. IR (film): ν 1693, 1531, 1497, 1458, 1354, 1211, 1175,

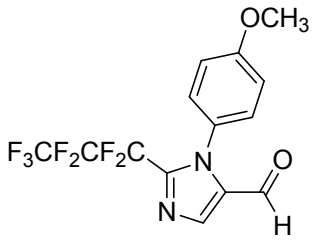
1138, 818, 766 cm^{-1}.

1-(4-methoxyphenyl)-2-(perfluoroethyl)-1H-imidazole-5-carbaldehyde (2v)



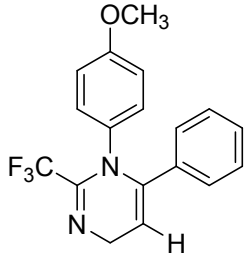
White solid, m. p.: 74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.87 (s, 1H), 7.20 (d, J = 12.0 MHz, 2H), 6.94 (d, J = 8.0 MHz, 2H), 3.81 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -82.30 (t, J = 5.6 MHz, 3F), -108.29 (s, 2F). ^{13}C NMR (400 MHz, $CDCl_3$) δ 179.0, 160.9, 139.6 (t, J = 54.5 MHz), 137.5, 135.2, 128.4, 126.1, 118.1 (qt, J_1 = 287.9 MHz, J_2 = 70.7 MHz), 114.5, 109.1 (tq, J_1 = 255.5 MHz, J_2 = 39.4 MHz), 55.6. HRMS (EI), Calcd. for $C_{13}H_9F_5N_2O_2$: 320.0584; Found: 320.0586. IR (film) ν 1691, 1610, 1514, 1448, 1325, 1301, 1255, 1224, 1175, 1039, 923, 839, 768 cm^{-1}. Anal. Calcd. for $C_{13}H_9F_5N_2O_2$: C,48.76; H, 2.83; N, 8.75; Found: C, 48.89; H, 2.89; N, 8.87.

1-(4-methoxyphenyl)-2-(perfluoropropyl)-1H-imidazole-5-carbaldehyde (2w)



White solid, m. p.: 117-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.89 (s, 1H), 7.19 (d, J = 8.0 MHz, 2H), 6.93 (d, J = 8.0 MHz, 2H), 3.81. ^{19}F NMR (282 MHz, $CDCl_3$) δ -80.05 (t, J = 16.9 MHz, 3F), 106.75 (q, J = 8.5 MHz, 2F), 124.93 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 160.9, 139.5 (t, J = 27.3 MHz), 137.7, 135.4, 128.5, 126.1, 117.6 (qt, J_1 = 288.9 MHz, J_2 = 34.3 MHz), 114.4, 110.0 (tt, J_1 = 328.3 MHz, J_2 = 32.3 MHz), 108.3 (tm, J_1 = 272.7 MHz), 55.6. HRMS (EI), Calcd. for $C_{14}H_9F_7N_2O_2$: 370.0552; Found: 370.0553.IR (film) ν 1692, 1514, 1450, 1342, 1255, 1230, 1209, 1117, 870 cm^{-1}. Anal. Calcd. for $C_{14}H_9F_7N_2O_2$: C,45.42; H, 2.45; N, 7.57; Found: C, 45.61; H, 2.51; N, 7.68.

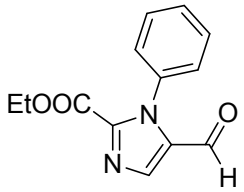
1-(4-methoxyphenyl)-6-phenyl-2-(trifluoromethyl)-1,4-dihydropyrimidine (2x)



Yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (s, 5H), 7.10 (d, J = 8.7 MHz, 2H), 6.68 (d, J = 8.7 MHz, 2H), 4.92 (t, J = 3.3 MHz, 1H), 4.51 (d, J = 2.1 MHz, 2H), 3.70 (s, 3H). ^{19}F NMR

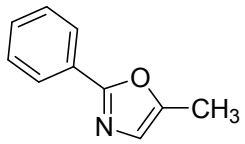
(282 Hz, $CDCl_3$): δ - 65.72 (s). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9, 147.2 (q, J = 32.8 MHz), 142.9, 135.2, 131.8, 131.4, 128.5, 128.1, 127.9, 117.7 (q, J = 277.1 MHz), 113.9, 103.6, 55.2, 46.0. MS (ESI): 333.3 (M + H^+). HRMS (ESI), Calcd. for $C_{18}H_{16}F_3N_2O$: 333. 12092; Found: 333.12185. IR (neat): ν 2941, 2839, 1638, 1509, 1337, 1248, 1196, 1165, 1142, 1037, 700 cm^{-1}.

Ethyl 5-formyl-1-phenyl-1H-imidazole-2-carboxylate (2y)



White solid, m. p.: 102-104 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.98 (s, 1H), 7.54 (m, 3H), 7.32 (m, 2H), 4.29 (q, J = 7.2 MHz, 2H), 1.26 (t, J = 7.2 MHz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 179.3, 157.7, 141.1, 138.1, 135.5, 135.0, 129.9, 129.3, 127.0, 62.2, 13.9. MS (EI), m/e (%): 244 (M^+, 40), 77 (100), 144 (97), 117 (75). IR (film) ν 2988, 1723, 1688, 1470, 1348, 1217, 810 cm^{-1}. Anal. Calcd. for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47; Found: C, 63.88; H, 5.19; N, 11.32.

5-methyl-2-phenyl-1H-imidazole (2z)

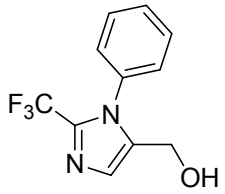


Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (m, 2H), 7.36 (m, 3H), 6.76 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 149.0, 130.1, 128.8, 127.5, 127.1, 126.0, 123.8 11.1. HRMS (EI), Calcd. for $C_{10}H_9NO$: 159.0684; Found:159.0683. IR (neat) ν 1574, 1511, 1455, 1367, 1234, 1183, 1204, 973, 764 cm^{-1}.

VII. General Procedure for the Synthesis of 5-Hydroxymethyl Imidazole

In an ice-water bath, $NaBH_4$ (380 mg, 5.0 equiv) was added in batches to a solution of *N*-phenyl 2-trlfluoromethyl imidazole-5-carbaldehyde (2.0 mmol) in CH_3OH. The reaction was quenched by addition of water when the reaction came to the end, extracted with EtOAc. The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4, filtered finally. The filter was concentrated under vacuum,

and the crude product was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (2:1) as eluent to give the desired product.



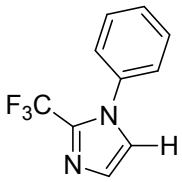
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 3H), 7.30 (m, 2H), 7.11 (s, 1H), 4.35 (s, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.26 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1 (q, J = 39.4 MHz), 136.4, 134.0, 130.2, 129.4, 127.6, 127.5, 118.5 (q, J = 271.7 MHz), 53.8; HRMS (EI) Calcd for $C_{11}H_9F_3N_2O$: 242.0667, found: 242.0668; IR (neat) ν 3455 (broad), 1585, 1513, 1430, 1308, 1255, 1176, 1222, 965, 776 cm^{-1}.

VIII. General Procedure for the Synthesis of 2-Fluoroalkyl Imidazole

Under argen atmosphere, to a Schlenk tube with a stirring bar was added KO*t*-Bu (3.0 equiv) and a solution of 2-fluoroalkyl imidazole-5-carbaldehyde (1.0 mmol) in DMF (5.0 mL). The system was then heated to 45 ℃ and monitored by TLC. The reaction was quenched by saturated NH_4Cl when the reaction came to the end, extracted with EtOAC. The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4, filtered finally. The filtrate was concentrated under vacuum, and the crude product was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (8:1) as eluent to give the desired product.

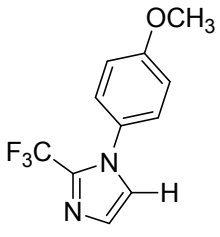
IX. Characterization for the 2-Fluoroalkyl Imidazole

1-phenyl-2-(trifluoromethyl)-1H-imidazole (5a)



White semisolid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (m, 3H), 7.38 (m, 2H), 7.25 (s, 1H), 7.18 (s, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.58 (s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.25, 135.95 (q), 129.70, 129.43, 128.67, 126.09, 125.13, 118.68 (q, J = 268.5 MHz); HRMS(EI) Calcd for $C_{10}H_7F_3N_2$: 212.0561, Found: 212.0562; IR (neat): ν 2960, 2929, 1598, 1524, 1499, 1444, 1307, 1241, 1192, 1133, 980, 768, 694 cm^{-1}.

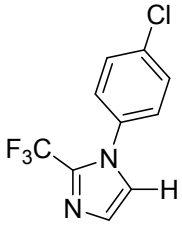
1-(4-methoxyphenyl)-2-(trifluoromethyl)-1H-imidazole (5b)



White solid, m. p.: 46-47 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26

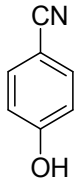
(m, 4H), 7.22, (s, 1H), 7.14 (s, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.66 (s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.86, 136.16 (q, *J* = 39.26 MHz), 133.74, 129.95, 128.61, 125.85, 125.24, 118.75 (q, *J* = 268.78 MHz), 21.18; HRMS(EI) Calcd for $C_{11}H_9F_3N_2$: 226.0718, Found: 226.0719; IR (film): ν 2921, 1517, 1476, 1446, 1308, 1238, 1194, 1127, 827, 781, 536 cm^{-1}.

1-(4-chlorophenyl)-2-(trifluoromethyl)-1H-imidazole (5c)



Light yellow semisolid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 12.0 MHz, 2H), 7.32 (d, *J* = 12.0 MHz, 2H), 7.25 (s, 1H), 7.15 (s, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.56 (s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.14 (q, *J* = 39.26 MHz), 135.87, 134.69, 129.71, 129.01, 127.43, 125.01, 118.58 (q, *J* = 276.33 MHz); HRMS(EI) Calcd for $C_{10}H_6ClF_3N_2$: 246.0172, Found: 246.0170; IR (neat): ν 3142, 3111, 1650, 1501, 1444, 1308, 1237, 1193, 1127, 1018, 980, 917, 841, 781, 537 cm^{-1}.

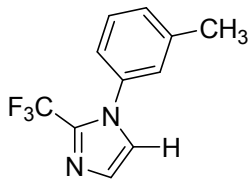
4-hydroxybenzonitrile (5e)



White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (d, *J* = 12.0 MHz, 2H), 6.94 (d, *J* = 12.0 MHz, 2H), 6.51 (broad, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.2, 134.4, 119.3, 116.5, 103.1.

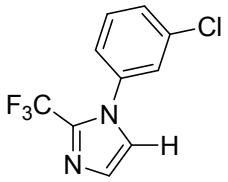
1-(m-tolyl)-2-(trifluoromethyl)-1H-imidazole (5f)

Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (m, 1H), 7.31 (m, 1H), 7.22 (s, 1H), 7.16 (m, 3H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.61 (s); ^{13}C NMR (151 MHz, $CDCl_3$)



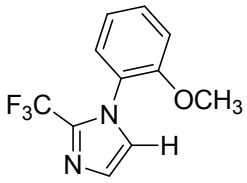
δ 139.67, 136.22, 136.06 (q, *J* = 39.26 MHz), 130.40, 129.15, 128.62, 126.62, 125.16, 123.11, 118.75 (q, *J* = 270.29 MHz), 21.23; HRMS(EI) Calcd for $C_{11}H_9F_3N_2$: 226.0718, Found: 226.0720; IR (neat): ν 2928, 1612, 1525, 1496, 1453, 1312, 1242, 1191, 1132, 1020, 918, 790, 696 cm^{-1}.

1-(3-chlorophenyl)-2-(trifluoromethyl)-1H-imidazole (5g)



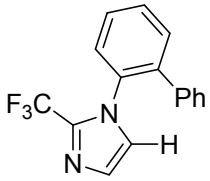
Light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.40 (m, 1H), 7.29 (m, 1H), 7.24 (s, 1H), 7.17 (s, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.54 (s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.21, 136.07 (q, *J* = 39.26 MHz), 135.15, 130.46, 130.04, 129.07, 126.47, 124.95, 124.45, 118.59 (q, *J* = 270.29 MHz); HRMS(EI) Calcd for $C_{10}H_6ClF_3N_2$: 246.0172, Found: 246.0171; IR (neat): ν 3141, 1696, 1529, 1488, 1449, 1312, 1246, 1185, 1131, 998, 785, 688 cm^{-1}.

1-(2-methoxyphenyl)-2-(trifluoromethyl)-1H-imidazole (5h)



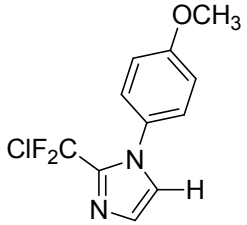
White semisolid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (m, 1H), 7.29 (m, 1H), 7.22 (m, 1H), 7.05 (m, 3H), 3.78 (s, 3H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -61.43 (s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.63, 136.62(q, *J* = 39.26 MHz), 131.25, 129.13, 128.49, 128.21, 125.35, 120.46, 118.70 (q, *J* = 270.29 MHz), 111.89, 55.73; HRMS(EI) Calcd for $C_{11}H_9F_3N_2O$: 242.0667, Found: 242.0666; IR (neat): ν 2938, 1602, 1509, 1471, 1440, 1286, 1244, 1188, 1132, 1025, 757 cm^{-1}.

1-([1,1'-biphenyl]-2-yl)-2-(trifluoromethyl)-1H-imidazole (5i)



White solid, m. p.: 89-92 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (m, 1H), 7.50 (m, 2H), 7.41 (m, 1H), 7.27 (m, 3H), 7.08 (m, 2H), 7.02 (s, 1H), 6.82 (s, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.69 (s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.29, 137.25, 136.29 (q, *J* = 39.26 MHz), 133.83, 131.17, 130.14, 128.53, 128.40, 128.21, 128.09, 127.98, 127.78, 125.73, 118.68 (q, *J* = 270.29 MHz); HRMS(EI) Calcd for $C_{16}H_{11}F_3N_2$: 288.0874, Found: 288.0871; IR (film): ν 3064, 2927, 1522, 1486, 1446, 1306, 1237, 1191, 1133, 979, 768, 700 cm^{-1}.

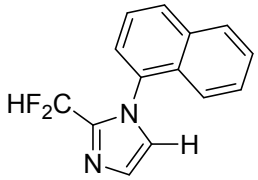
2-(chlorodifluoromethyl)-1-(4-methoxyphenyl)-1H-imidazole (5j)



White solid, m. p.: 71-73 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 12.0 MHz, 2H), 7.19 (s, 1H), 7.10 (s, 1H), 6.98 (d, *J* =

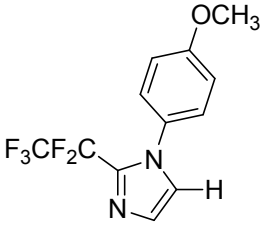
12.0 MHz, 2H), 3.87 (s, 3H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -45.88 (s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.31, 139, 88 (t, J = 32.47 MHz), 129.08, 128.13, 127.84, 125.77, 120.63 (t, J = 286.90 MHz), 114.30, 55.60; HRMS(EI) Calcd for $C_{11}H_9ClF_2N_2O$: 258.0371, Found: 258.0373; IR (film): ν 1610, 1517, 1467, 1297, 1255, 1218, 1122, 992, 899, 837 cm^{-1}.

2-(difluoromethyl)-1-(naphthalen-1-yl)-1H-imidazole (5k)



White solid, m. p.: 107-109 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (m, 2H), 7.63 (m, 4H), 7.34 (s, 1H), 7.29 (m, 1H), 7.22 (s, 1H), 6.60 (t, J = 78.0 MHz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.95 (dd); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.14 (t, J = 27.18 MHz), 138.58, 133.96, 132.47, 130.27, 128.80, 128.27, 127.87, 127.08, 125.37, 125.21, 124.95, 121.97, 108.89 (t, J = 237.07 MHz); HRMS(EI) Calcd for $C_{14}H_{10}F_2N_2$: 244.0812, Found: 244.0810; IR (film): ν 1692, 1597, 1483, 1440, 1299, 1185, 1072, 1037, 811, 775 cm^{-1}.

1-(4-methoxyphenyl)-2-(perfluoroethyl)-1H-imidazole (5l)



White solid, m. p.: 73-75 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (m, 3H), 7.14 (s, 1H), 6.97 (d, J = 12.0 MHz, 2H), 3.87 (s. 3H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -82.36 (s, 3F), -106.55 (s, 2F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.31, 135.02 (t, J = 28.69 MHz), 129.09, 128.13 (q), 127.65, 126.22, 118.42 (qt, J_1 = 286.90 MHz, J_2 = 35.49 MHz), 114.25, 109.33 (tq, J_1 = 252.93 MHz, J_2 = 39.26 MHz), 55.6; HRMS(EI) Calcd for $C_{12}H_9F_5N_2O$: 292.0635, Found: 292.0635; IR (film): ν 1511, 1442, 1257, 1234, 1194, 1098, 1040, 952, 911, 837, 767 cm^{-1}.

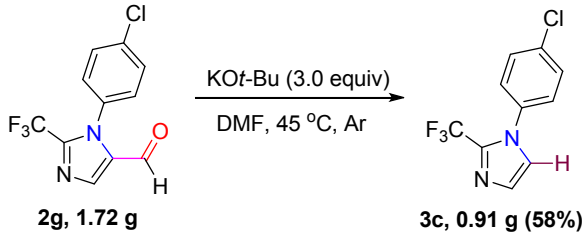
X. A Concise Route to Synthesize 3m on Gram Scale

(1)

1g, 2 g **2g, 1.72 g (82%)**

To a 250 mL of dry reactor was added $BiCl_3$ (24 mg, 0.076 mmol, 0.01 equiv), and the reactor was degassed and refilled with O_2 for three times. Then a solution of **1g** (2g, 7.69 mmol, 1,0 equiv) in acetone (80 mL) and a solution of phenol (1.45g, 11.5 mmol, 2.0 equiv) in acetone (40 mL) were added sequentially to the reactor. The system was then heated to 40 ℃ and monitored by TLC. The solvent was removed under vacuum when the reaction came to the end. The crude product was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (7:1) as the eluent to give 1.72 g (82%) of **2g**.

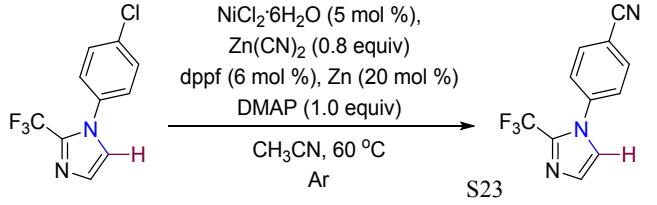
(2)



2g, 1.72 g **3c, 0.91 g (58%)**

A 100 mL of dry reactor with a stirring bar was degassed and refilled with argon for three times. Then KO*t*-Bu (2.12g, 18.9 mmol, 3.0 equiv) and a solution of **2g** (1.72 g, 6.31 mmol, 1.0 equiv) in DMF (40 mL) were added sequentially to the reactor. The system was then heated to 45 ℃ and monitored by TLC. The reaction was quenched by saturated NH_4Cl when the reaction came to the end, extracted with EtOAC. The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4, filtered finally. The filtrate was concentrated under vacuum, and the crude product was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (8:1) to give 0.91 g (58%) of **3c**.

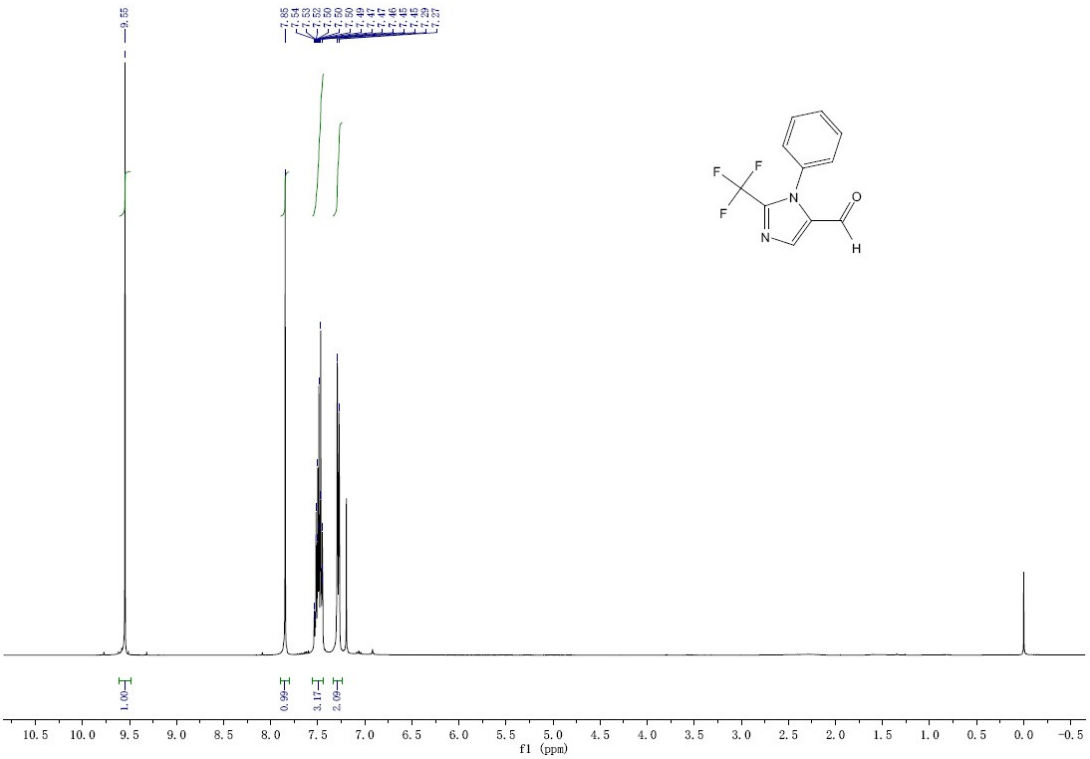
(3)

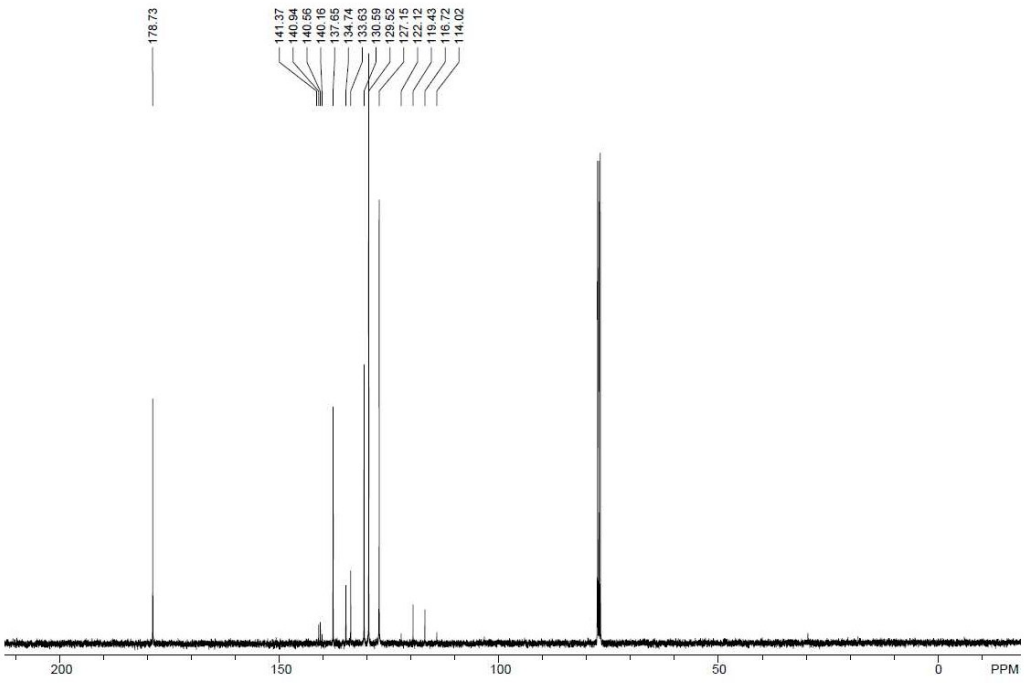


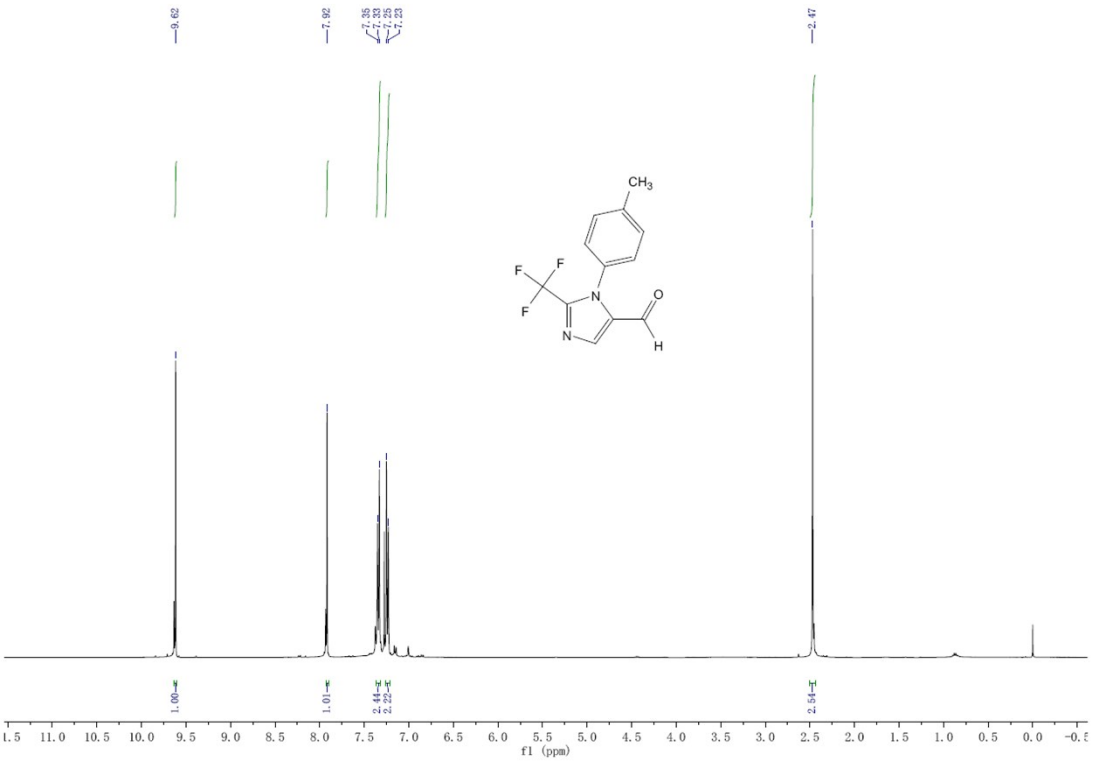
3c, 0.91 g **3m, 0.54 g (62%)**

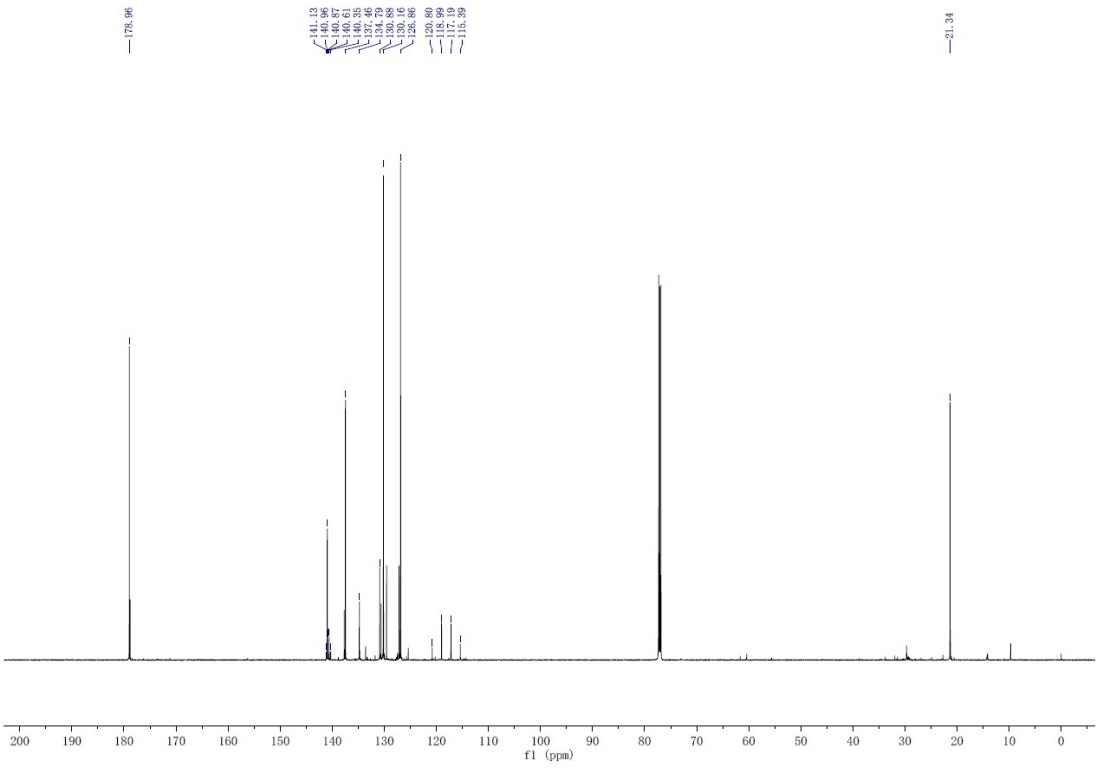
To a dry Schlenk tube with a stirring bar was added $NiCl_2 \cdot 6H_2O$ (44 mg, 0.19 mmol, 0.05 equiv), dppf (123 mg, 0.22 mmol, 0.06 equiv), Zn (48 mg, 0.74 mmol, 0.2 equiv), DMAP (452 mg, 3.7 mmol, 1.0 equiv), $Zn(CN)_2$ (348 mg, 2.96 mmol, 0.8 equiv), and the Schlenk tube was degassed and refilled with argon for three times. Then a solution of **3c** (0.91 g, 3.7 mmol, 1,0 equiv) in CH_3CN (25 mL) was added. The Schlenk tube was immersed into an oil bath preheated at 80 ℃ and monitored by TLC. The solvent was removed under vacuum when the reaction came to the end. The crude product was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (4:1) as the eluent to give 0.54 g (62%) of **3m** as a light yellow solid.

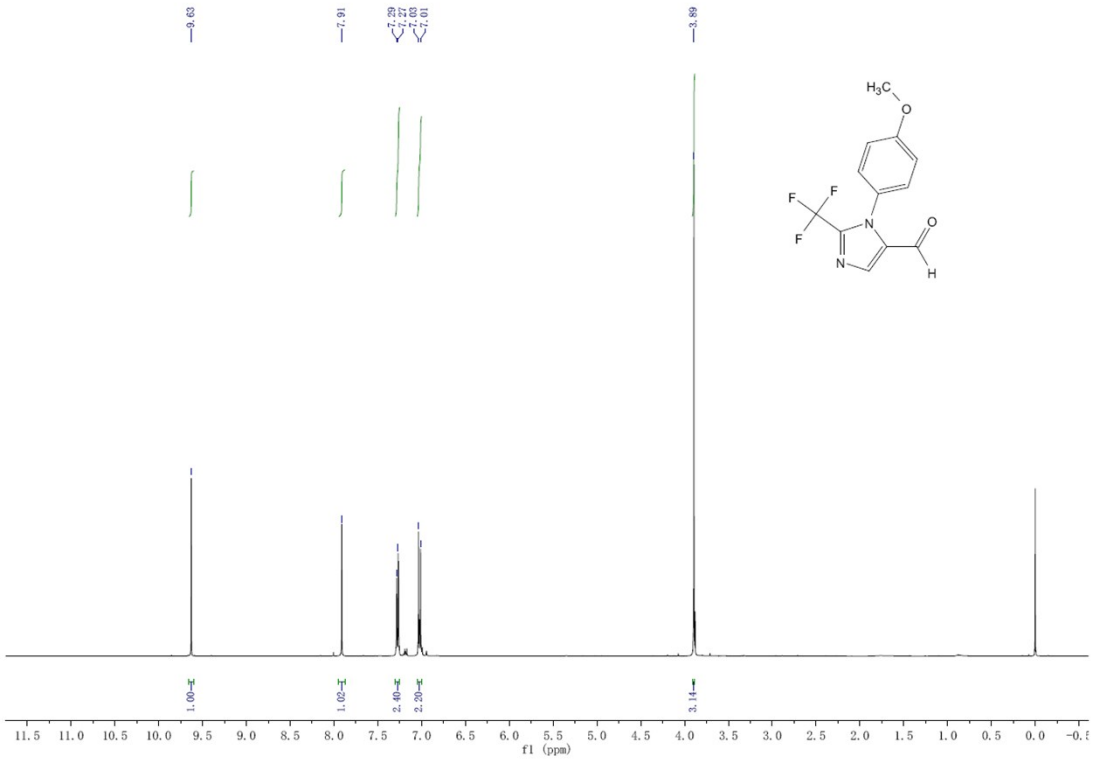
XI. NMR Spectra for the 2-Fluoroalkyl Imidazole Derivatives

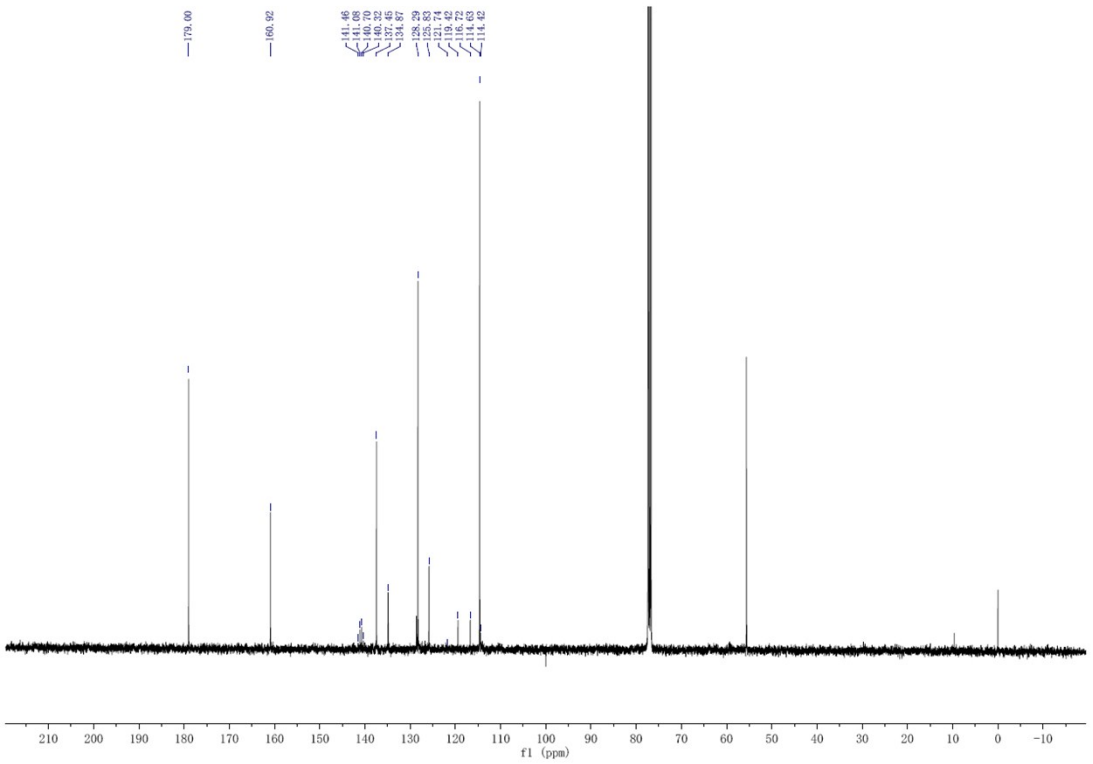

9.55
7.85
7.54
7.53
7.52
7.50
7.50
7.49
7.47
7.47
7.46
7.45
7.45
7.29
7.27
F
F
F
N
N
O
H
1.00
0.99
3.17
2.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

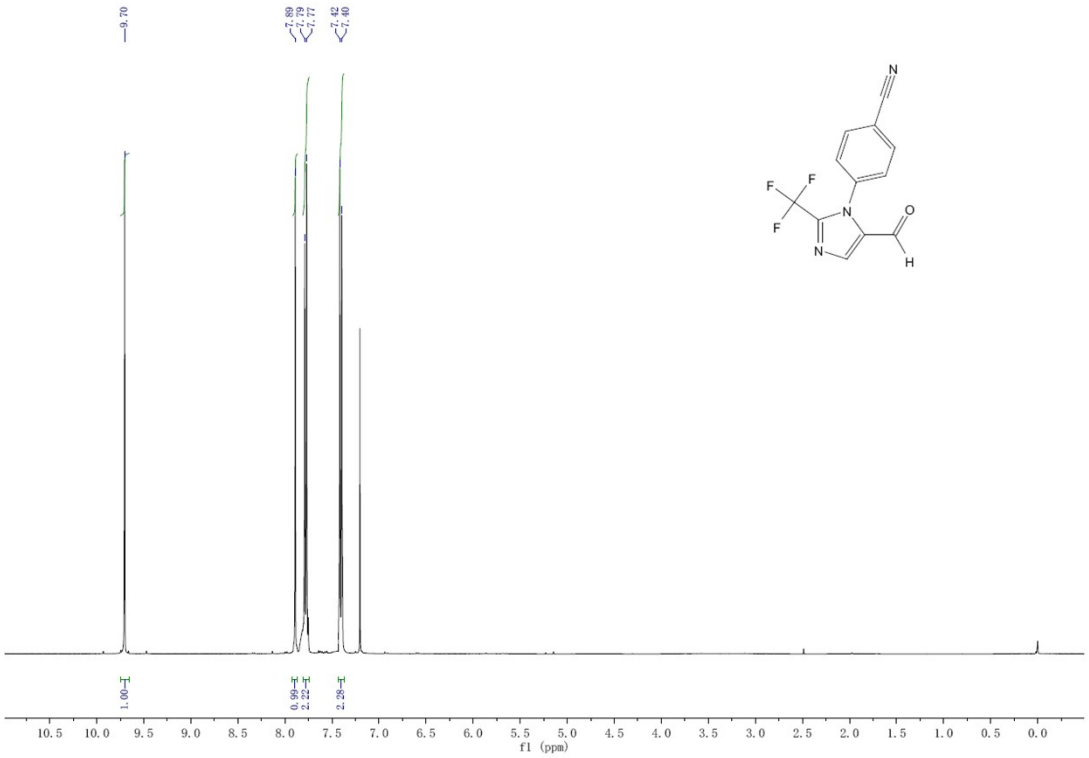

178.73
141.37
140.94
140.56
140.16
137.85
134.74
133.63
130.69
129.52
127.15
122.12
119.43
116.72
114.02
200
150
100
50
0
PPM

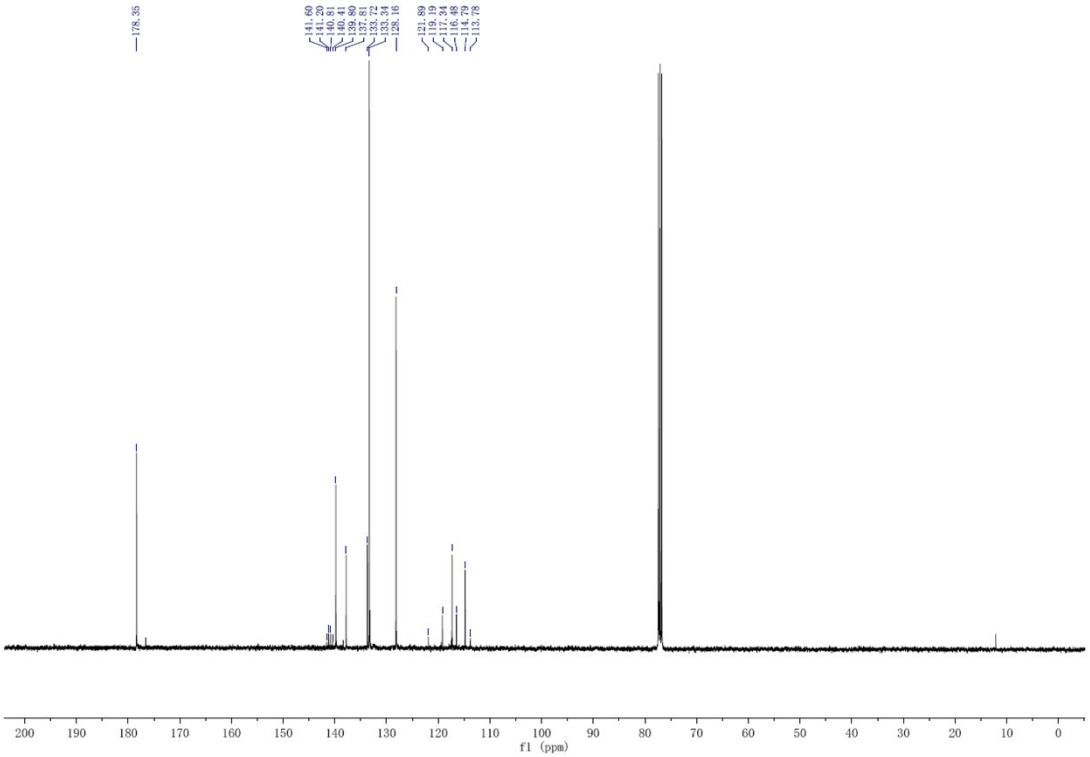

9.62
7.92
7.35
7.33
7.25
7.23
2.47
CH3
F
F
F
N
N
O
H
1.00
1.01
2.44
2.22
2.54
f1 (ppm)


178.96
141.13
140.96
140.87
140.61
140.35
134.46
134.79
130.88
130.16
126.86
120.80
119.69
117.19
115.39
21.34
f1 (ppm)


9.63
7.91
7.29
7.27
7.03
7.01
3.89
H3C
O
F
F
F
N
N
O
H
1.00
1.02
2.40
2.20
3.14
f1 (ppm)


179.00
160.92
141.46
141.08
140.70
140.32
137.45
134.87
128.29
125.53
121.74
119.42
116.72
114.63
114.42
f1 (ppm)


9.70
7.89
7.79
7.77
7.42
7.40
N
F
F
F
N
N
O
H
1.00
0.99
2.22
2.28
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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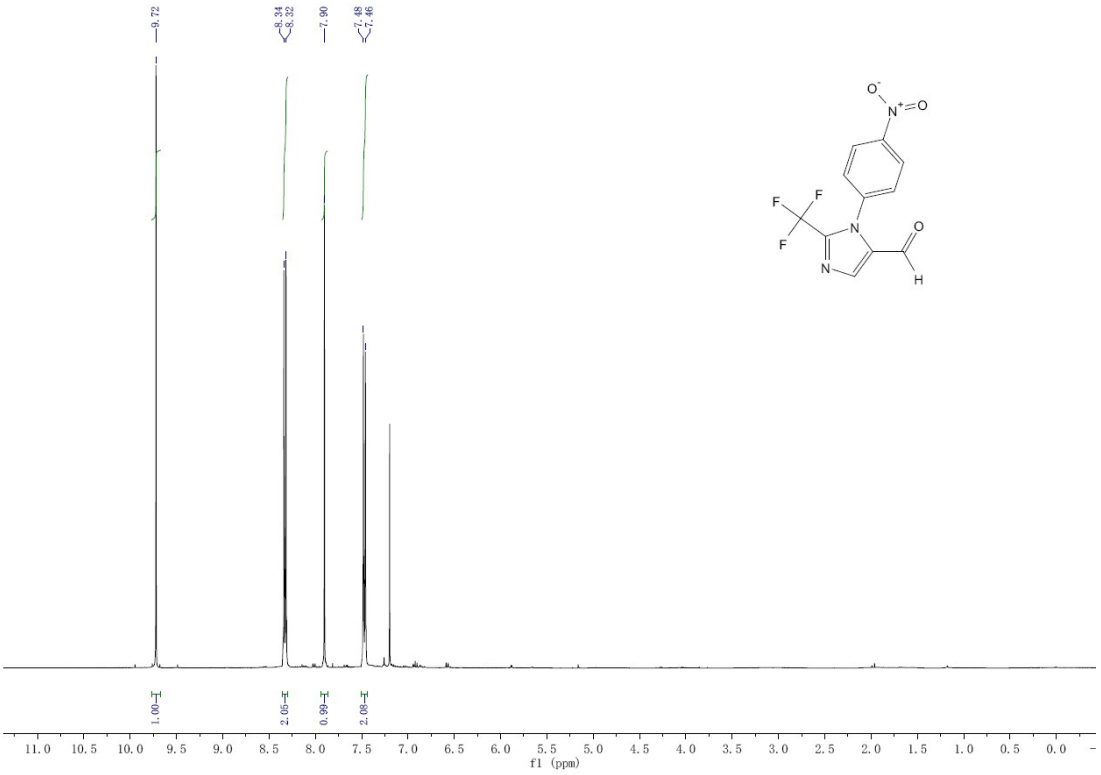
141.60
141.20
140.81
140.41
138.80
137.81
133.72
133.34
126.16
121.89
119.19
117.34
116.48
114.79
113.78
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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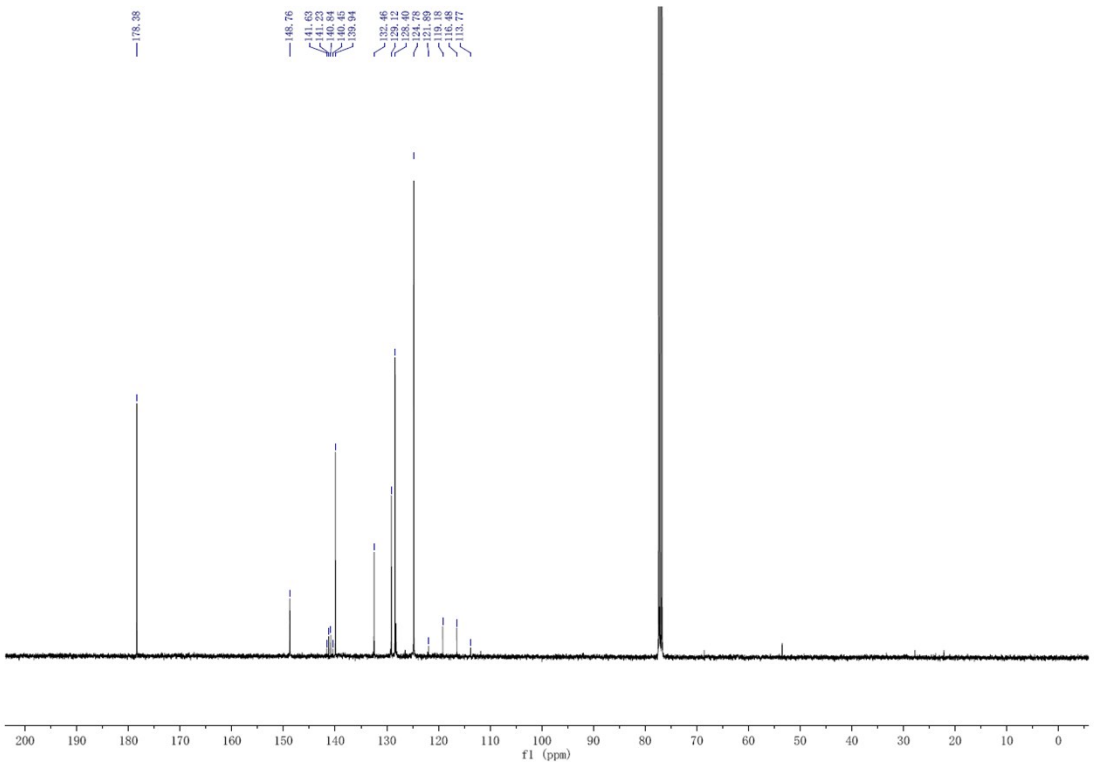
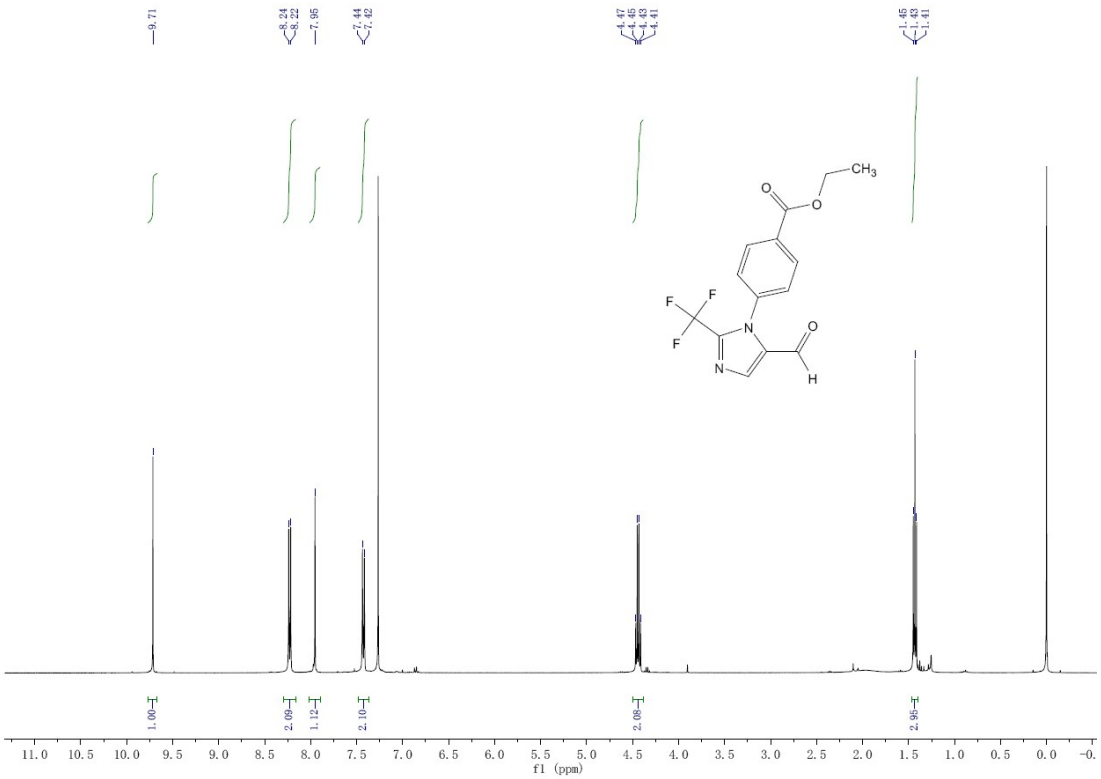
8.34
8.32
7.90
7.48
7.46
1.00
2.05
0.99
2.08
f1 (ppm)


178.38
148.76
141.63
141.23
140.84
140.45
139.94
132.46
129.12
128.40
124.78
121.89
119.18
116.48
113.77
f1 (ppm)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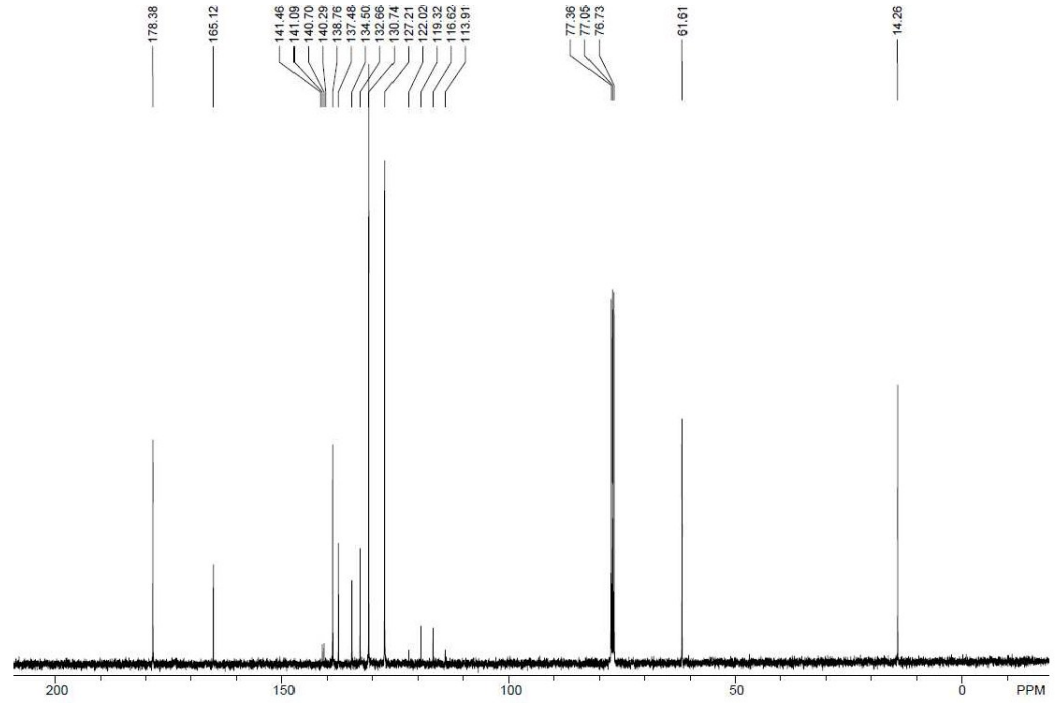
8.24
8.22
7.95
7.44
7.42
4.47
4.45
4.43
4.41
1.45
1.43
1.41
1.00
2.09
1.12
2.10
2.08
2.96
f1 (ppm)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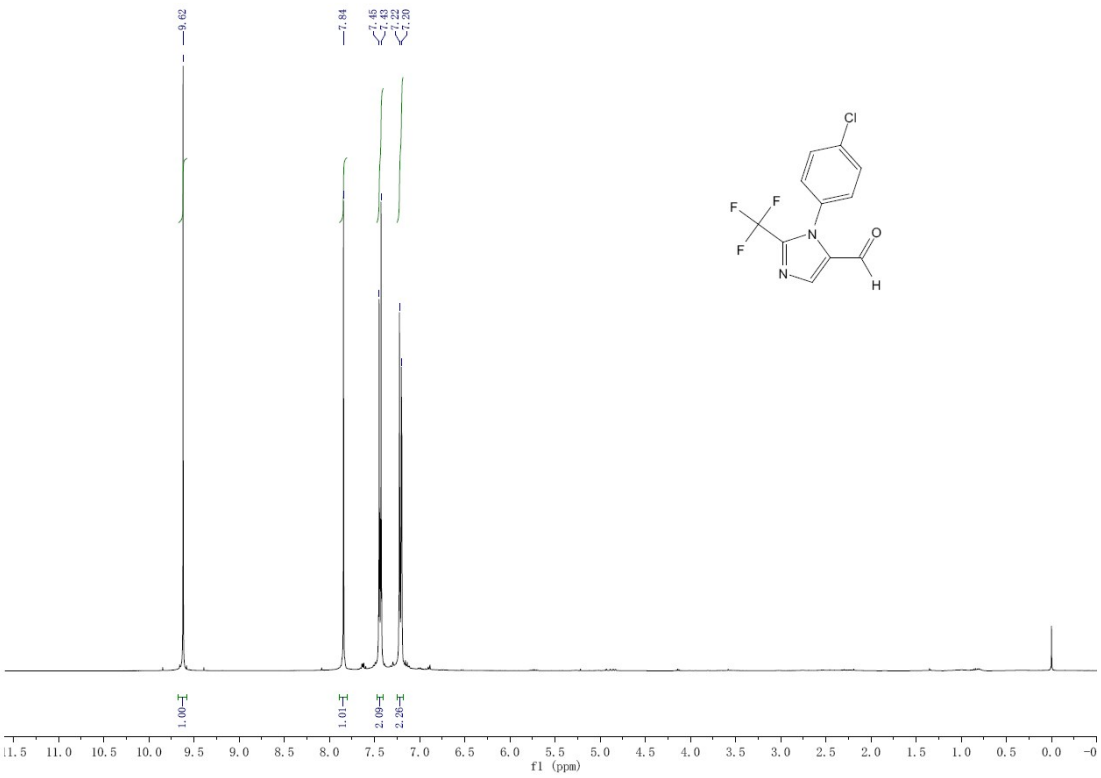
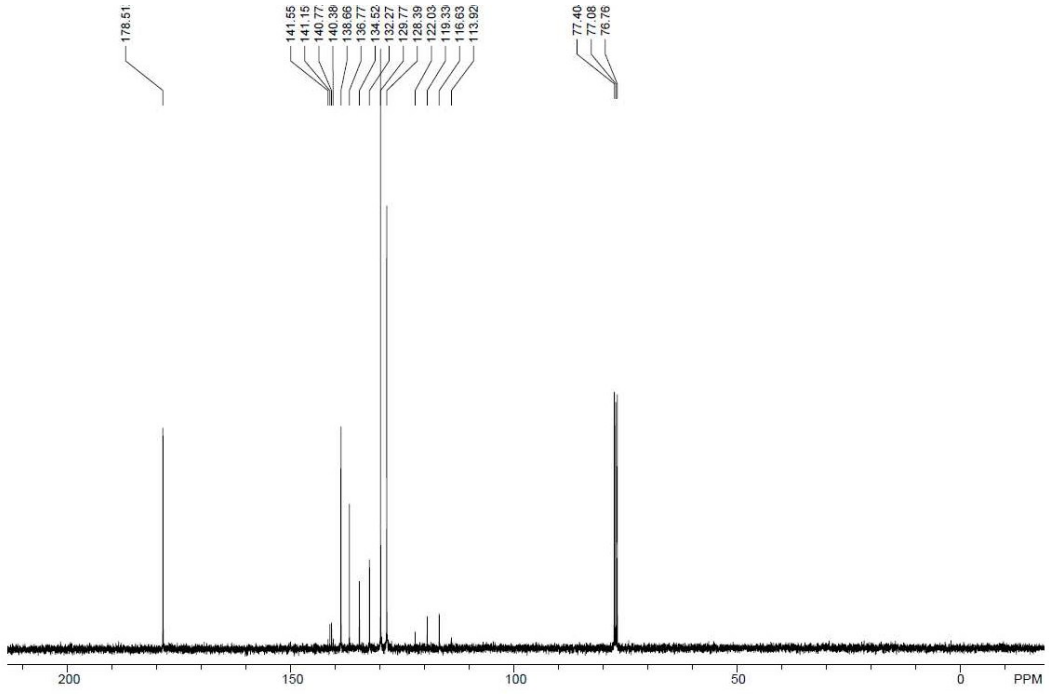
165.12
141.46
141.09
140.70
140.29
138.76
137.48
134.50
132.66
130.74
127.21
122.02
119.32
116.62
113.91
77.36
77.05
76.73
61.61
14.26
PPM


9.62
7.84
7.45
7.43
7.22
7.20
Cl
F
F
F
N
N
O
H
1.00
1.01
2.09
2.26
f1 (ppm)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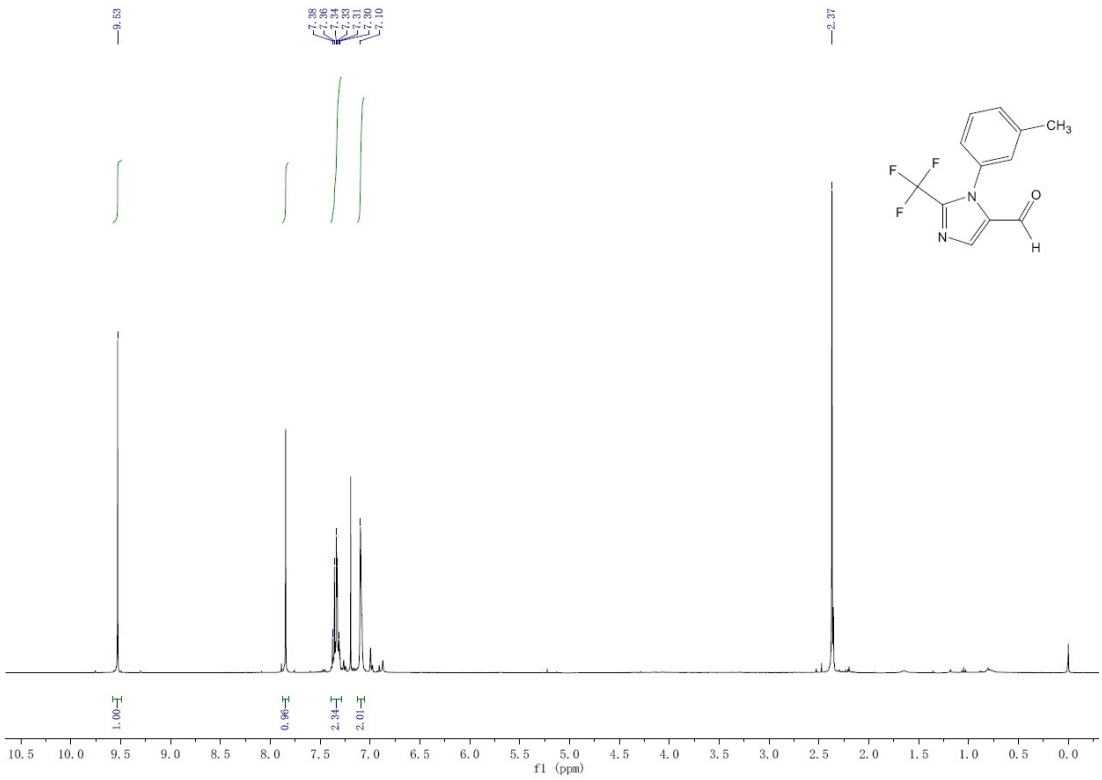
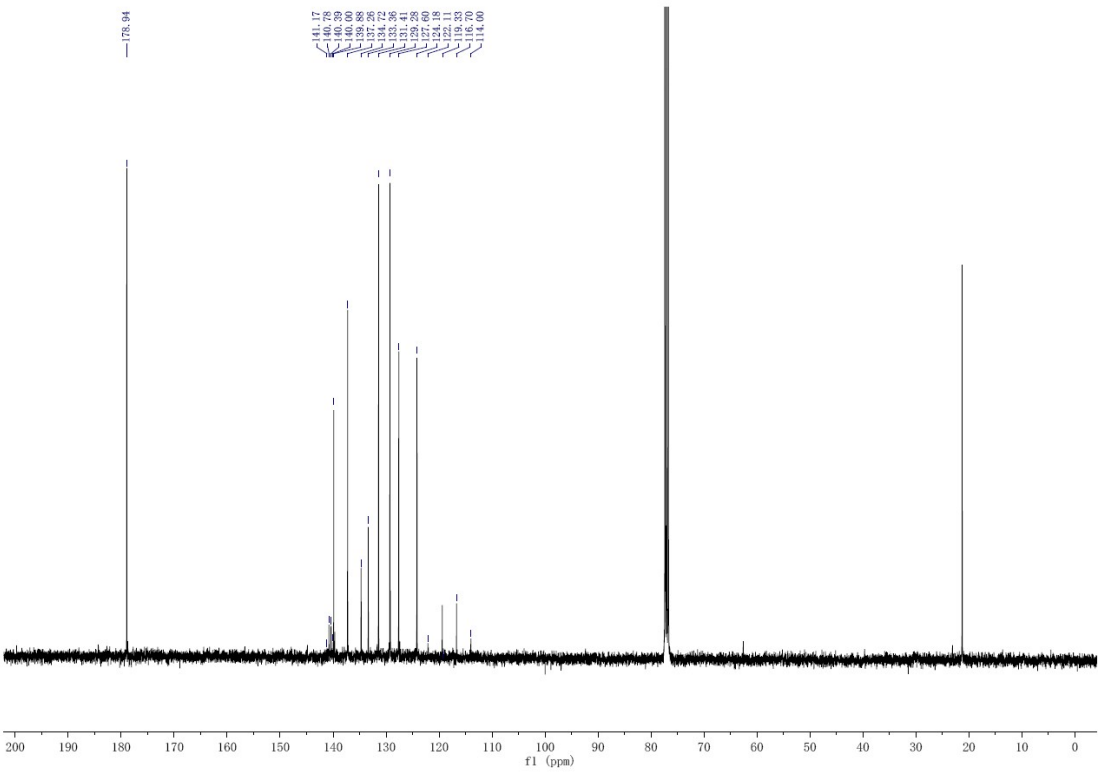
141.55
141.15
140.77
140.39
138.66
136.77
134.52
132.27
129.77
128.39
122.03
119.33
116.63
113.92
77.40
77.08
76.76
200
150
100
50
0
PPM


9.53
7.38
7.35
7.34
7.33
7.31
7.30
7.10
2.37
CH3
F
F
F
N
N
O
H
1.00
0.96
2.34
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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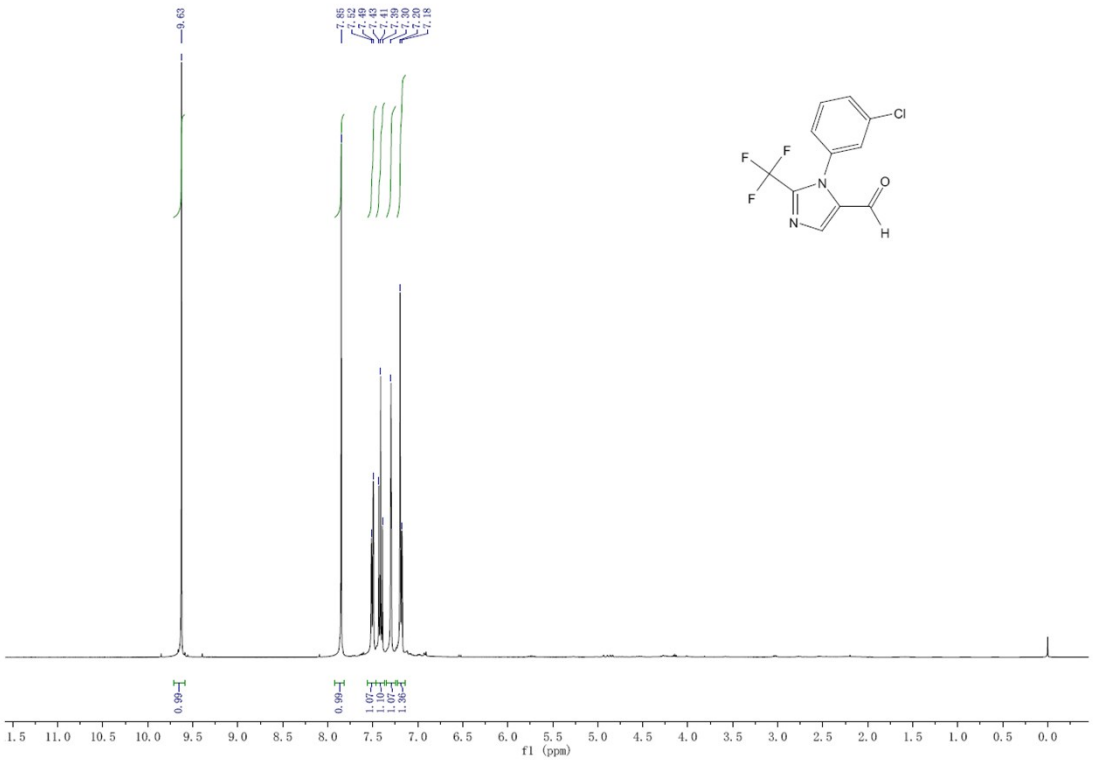
141.17
140.78
140.39
140.00
139.88
137.26
134.72
133.36
131.41
129.28
127.69
124.18
122.11
119.33
116.70
114.60
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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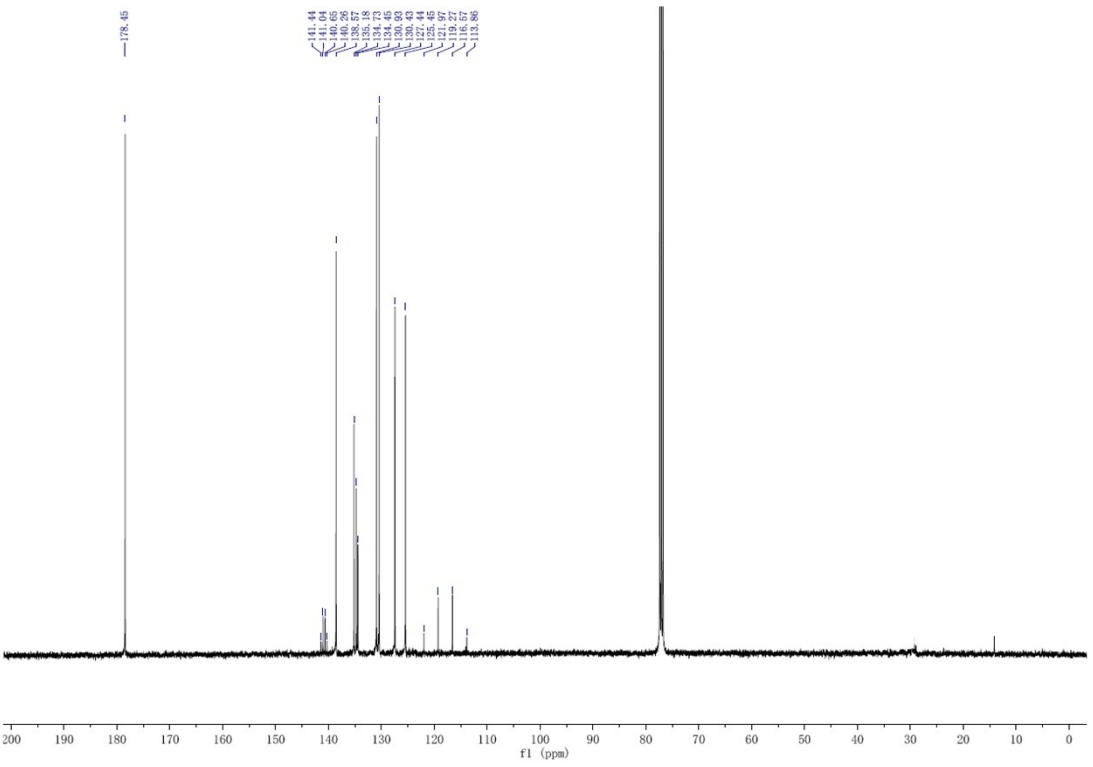
7.85
7.52
7.49
7.43
7.41
7.39
7.20
7.18
Cl
F
F
F
N
N
O
H
0.99
0.99
1.07
1.07
1.36
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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141.04
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138.57
135.38
134.73
134.45
130.93
130.43
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121.97
119.27
116.57
113.86
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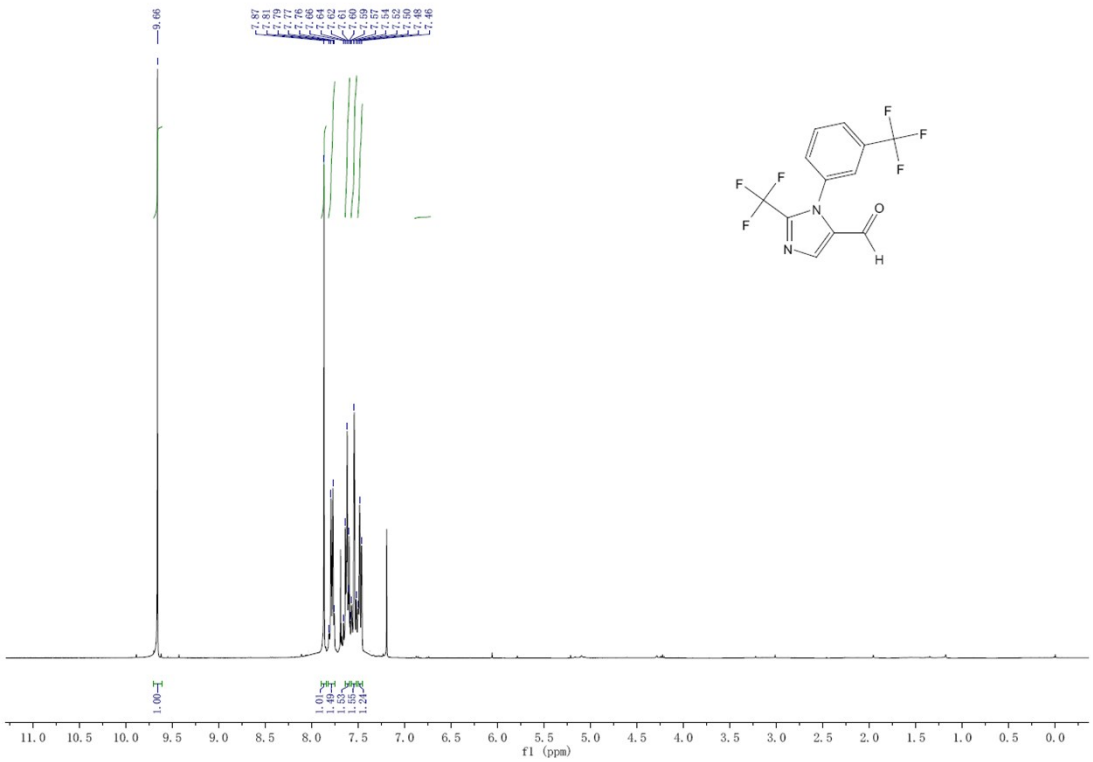
f1 (ppm)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7.87
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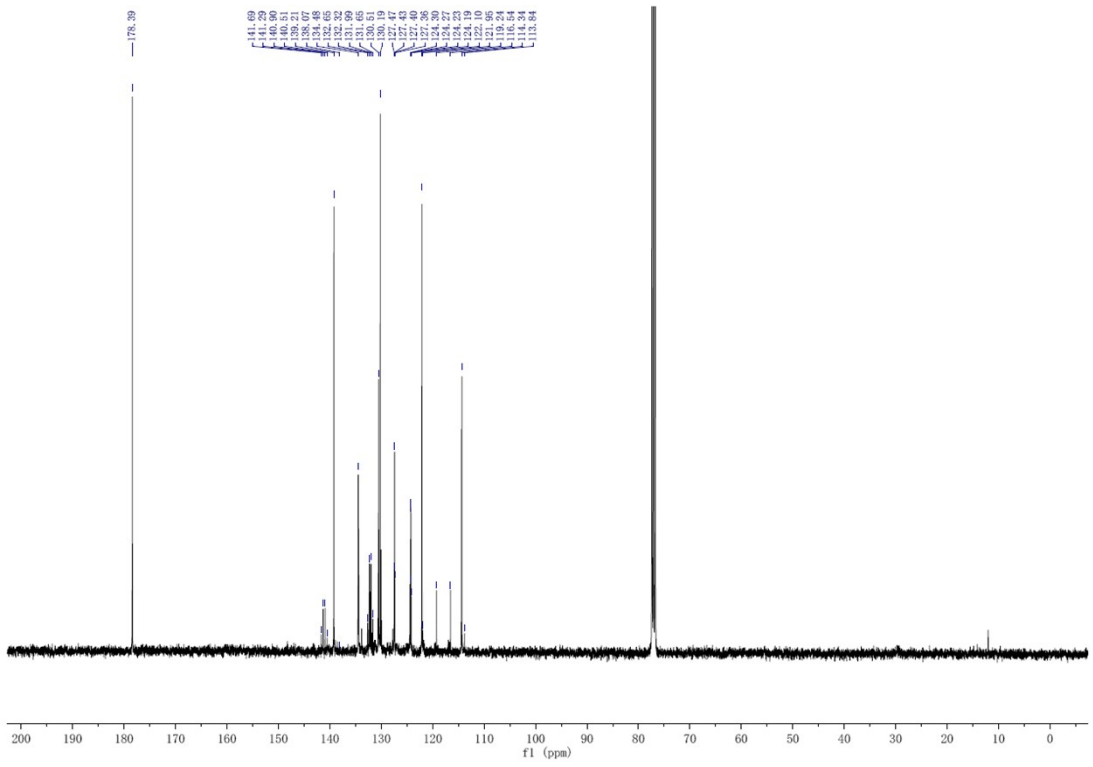
7.77
7.76
7.66
7.64
7.62
7.61
7.60
7.59
7.57
7.54
7.52
7.50
7.48
7.46
F
F
F
F
F
N
N
O
H
1.00
1.01
1.49
1.53
1.65
1.24
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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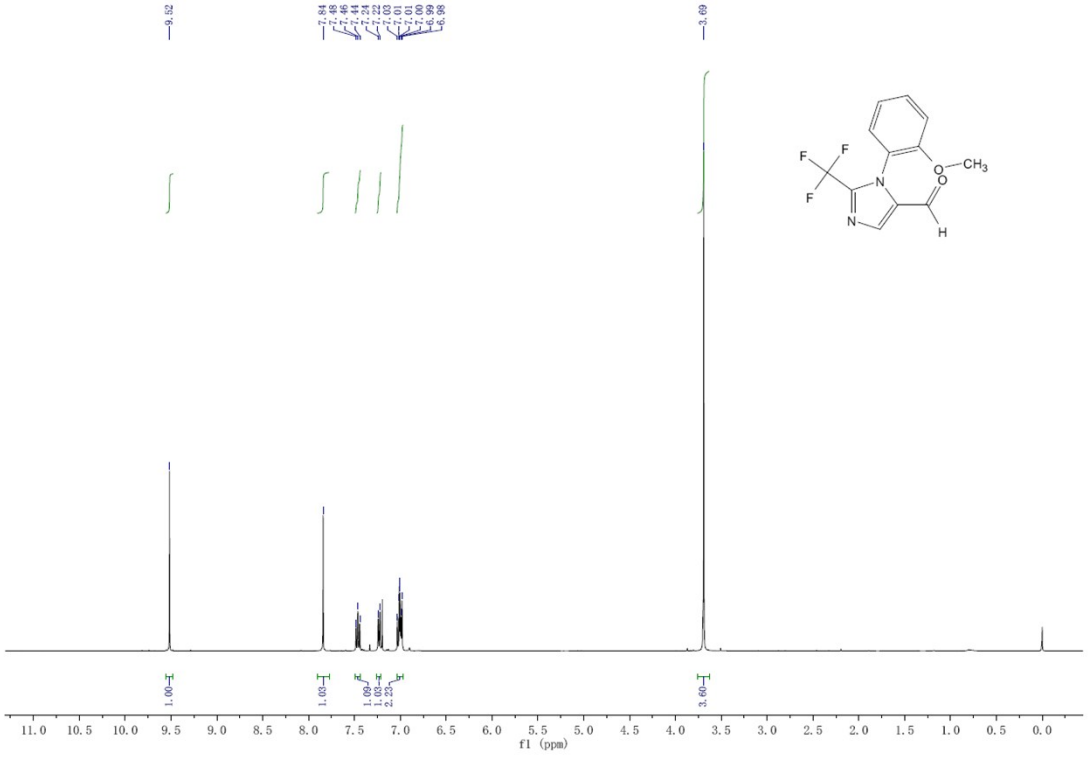
141.29
140.90
140.51
139.21
138.07
134.48
132.65
132.32
131.99
131.65
130.51
130.19
127.47
127.43
127.40
127.36
124.30
124.27
124.23
124.19
122.10
121.95
119.24
116.54
114.24
113.84
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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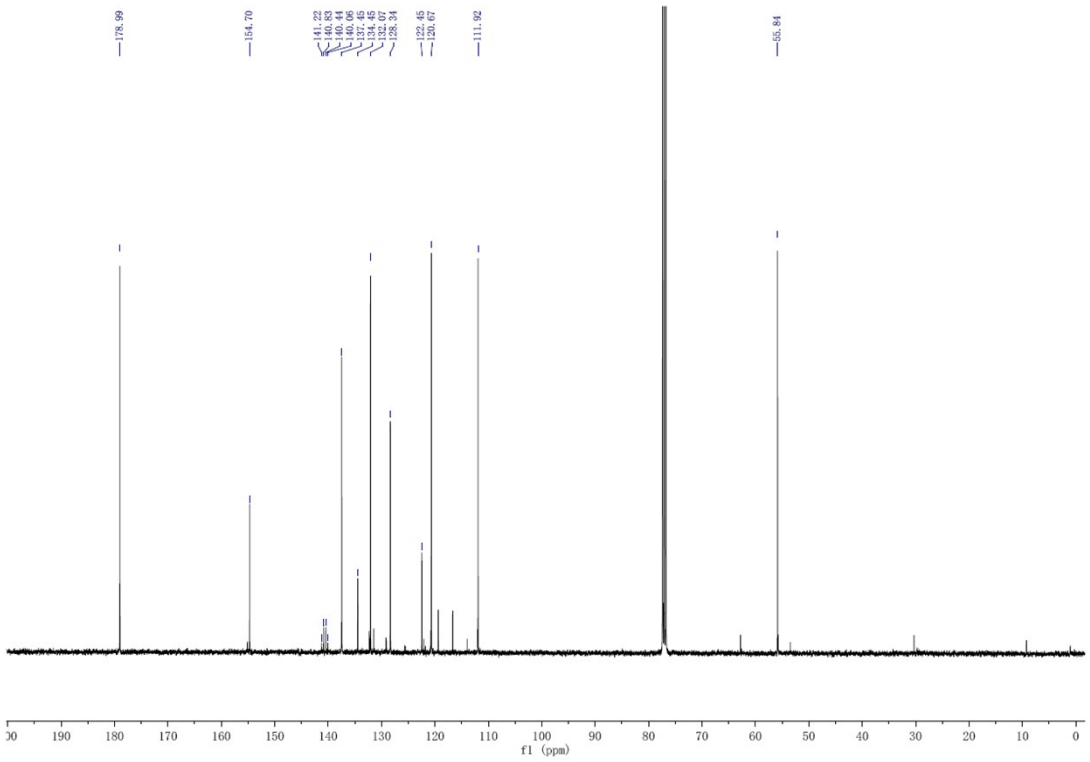
7.84
7.48
7.46
7.44
7.23
7.22
7.03
7.01
7.00
6.99
6.98
3.69
F
F
F
N
N
O
CH3
O
H
1.00
1.03
1.08
1.04
2.23
3.60
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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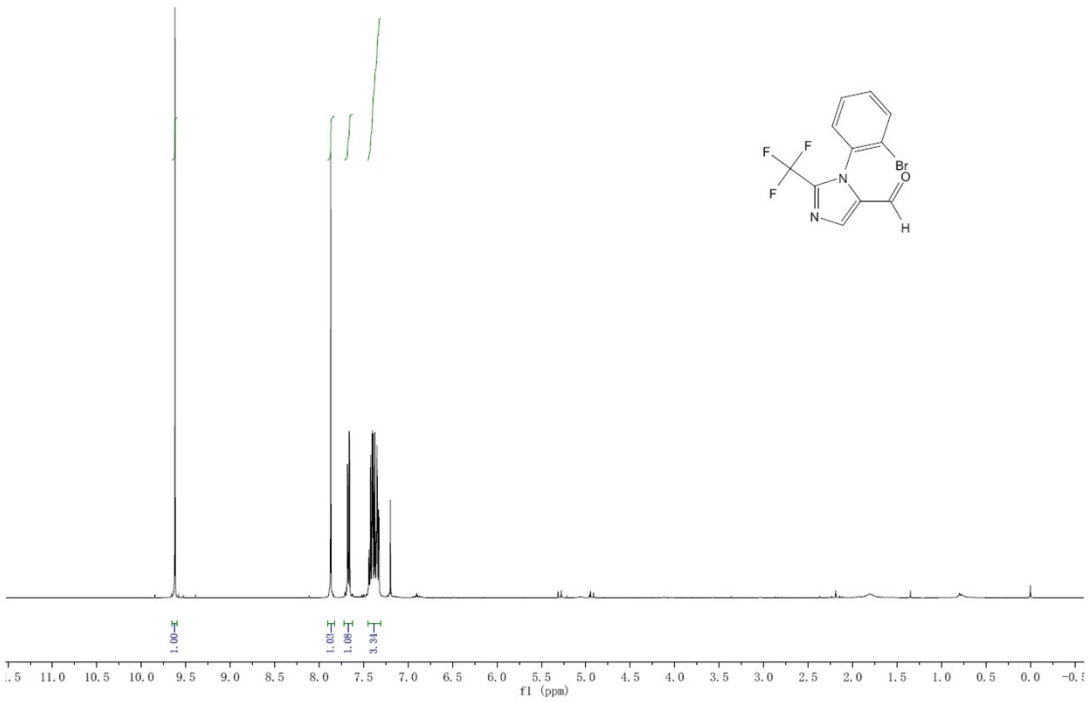
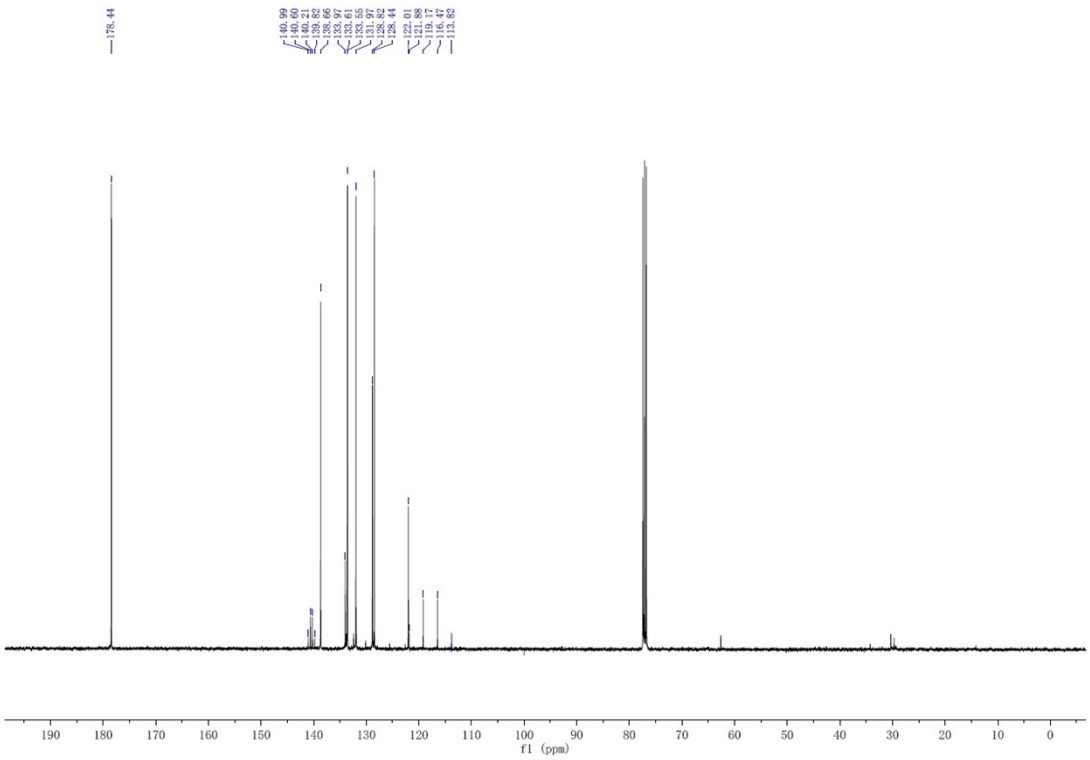
154.70
141.22
140.83
140.44
140.06
137.45
134.45
132.07
128.94
122.45
120.67
111.92
55.84
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F
F
F
N
N
Br
O
H
1.00
1.02
1.08
3.34
f1 (ppm)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140.99
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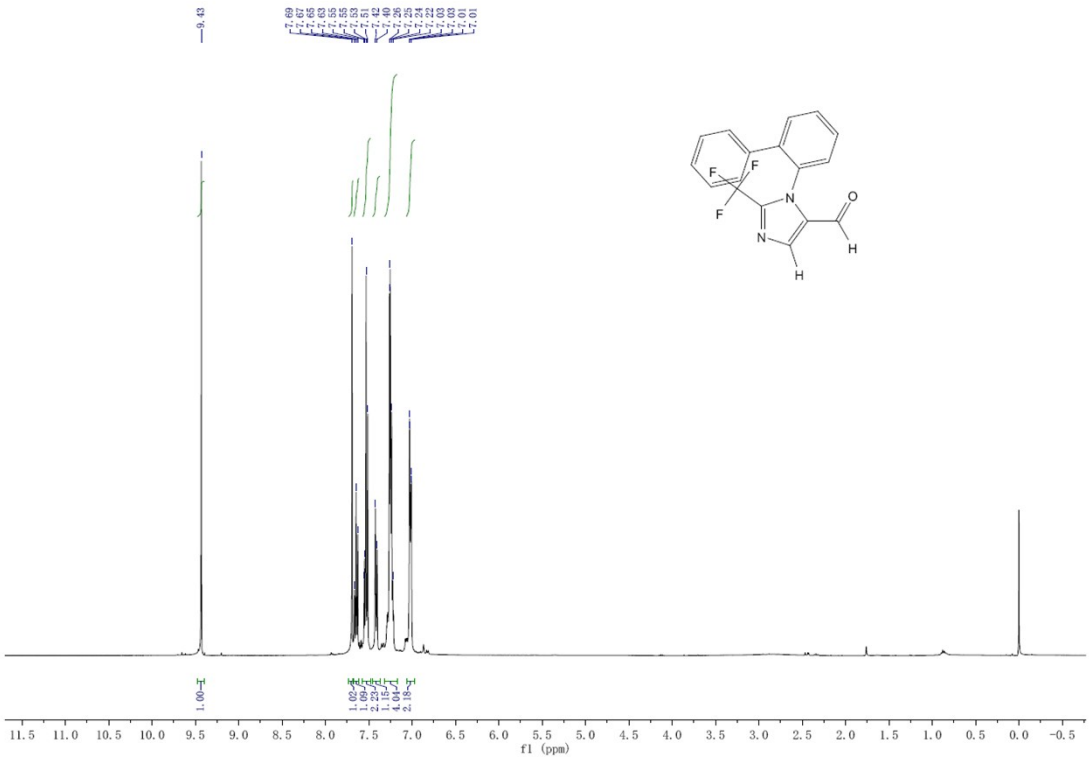
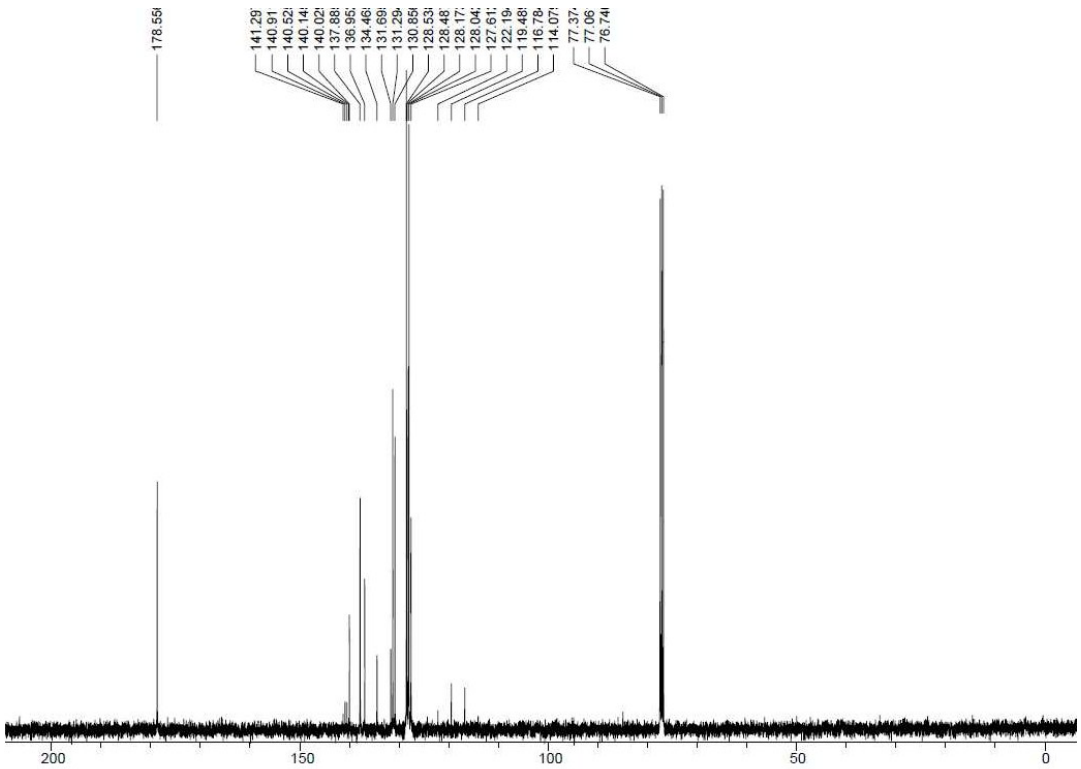
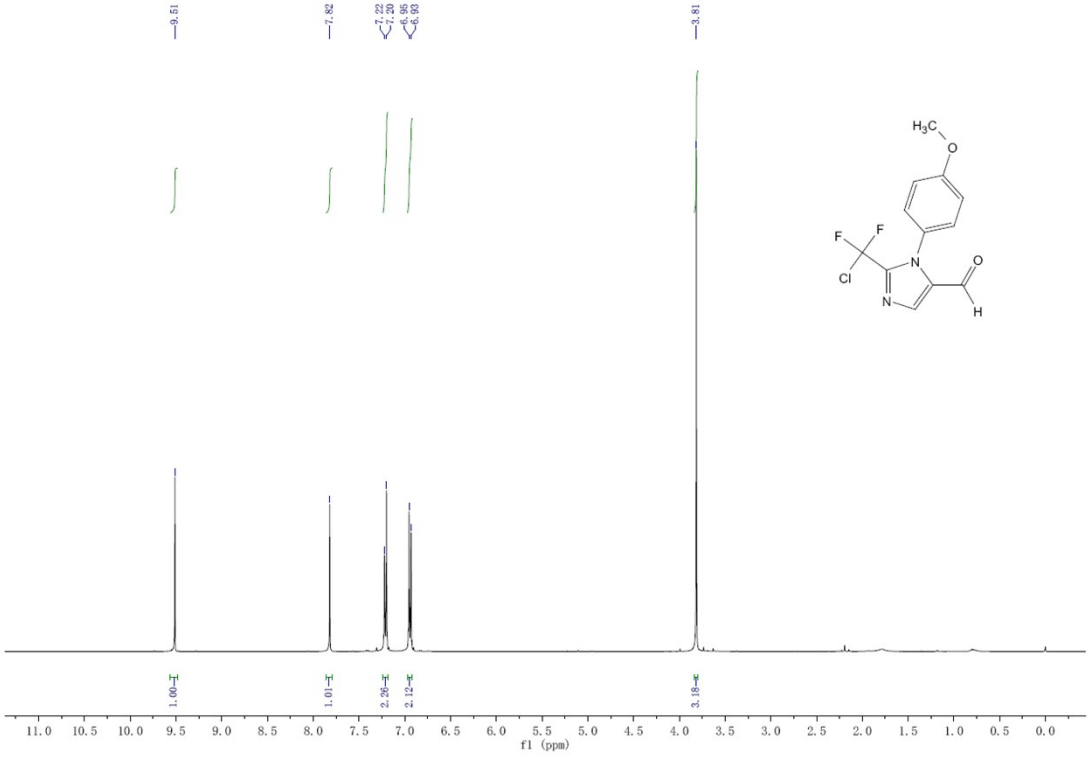
140.21
139.82
138.66
133.97
133.61
133.55
131.97
130.82
128.44
122.01
121.88
119.17
116.47
113.82
f1 (ppm)


F
F
F
N
N
O
H
H
f1 (ppm)


200
150
100
50
0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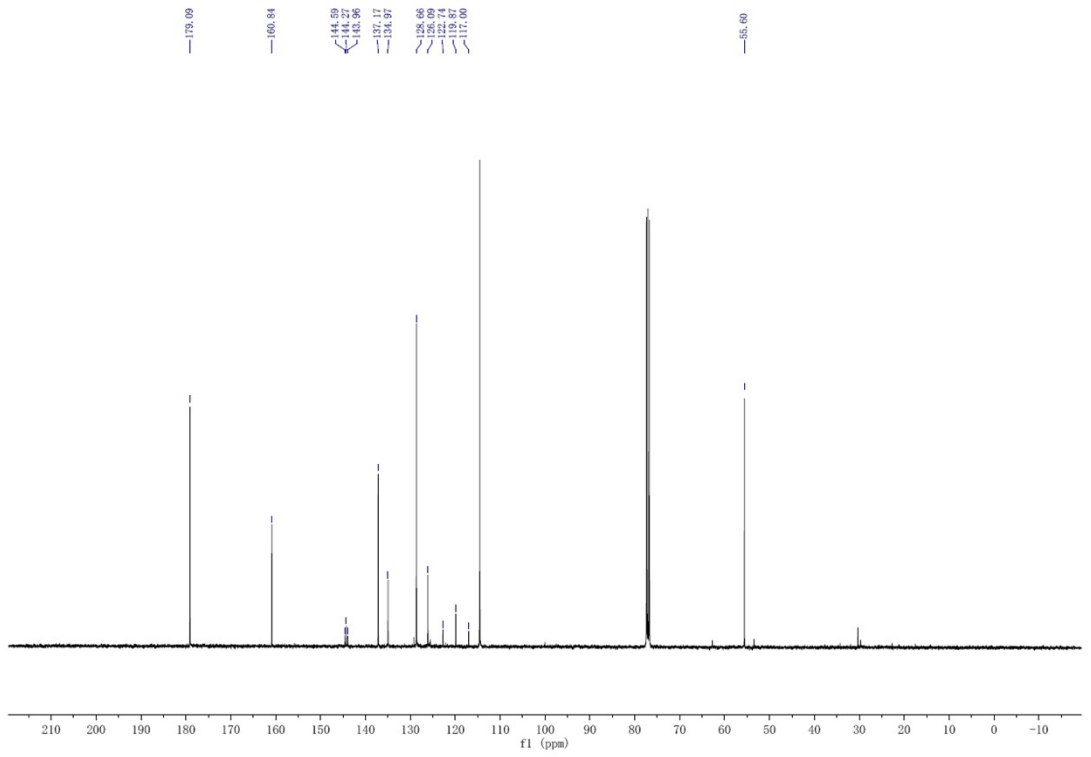
7.82
7.22
7.20
6.96
6.93
3.81
1.00
1.01
2.26
2.12
3.18
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
H3C
O
F
F
Cl
N
N
O
H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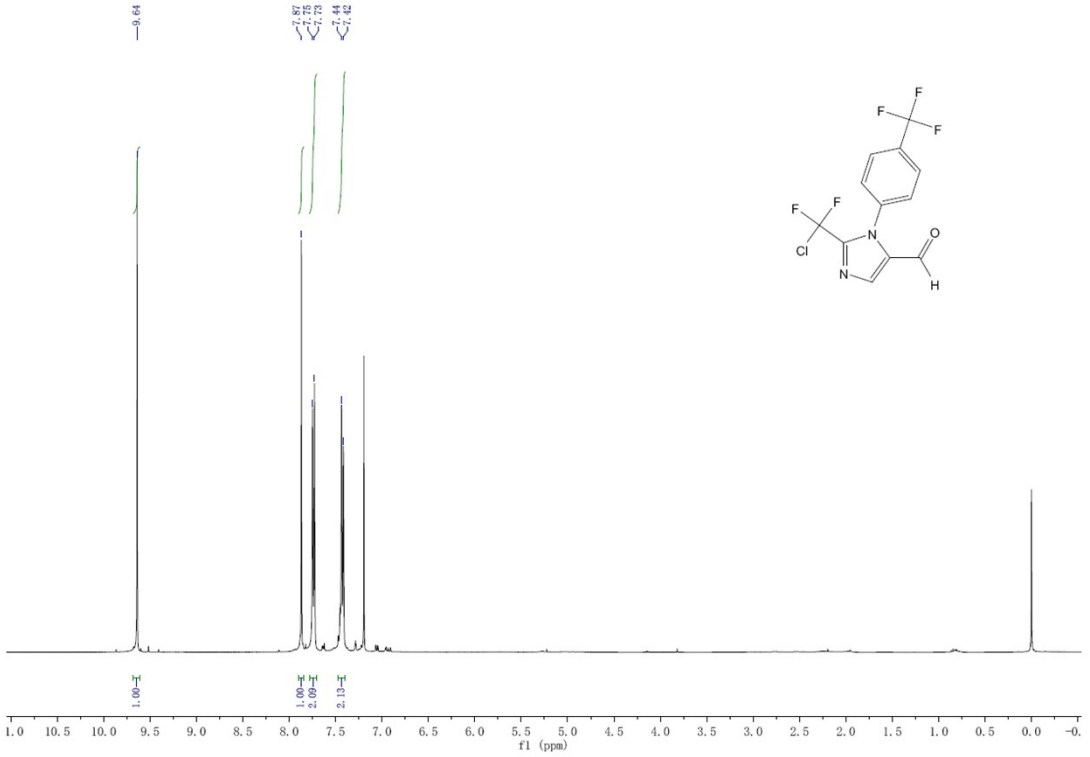
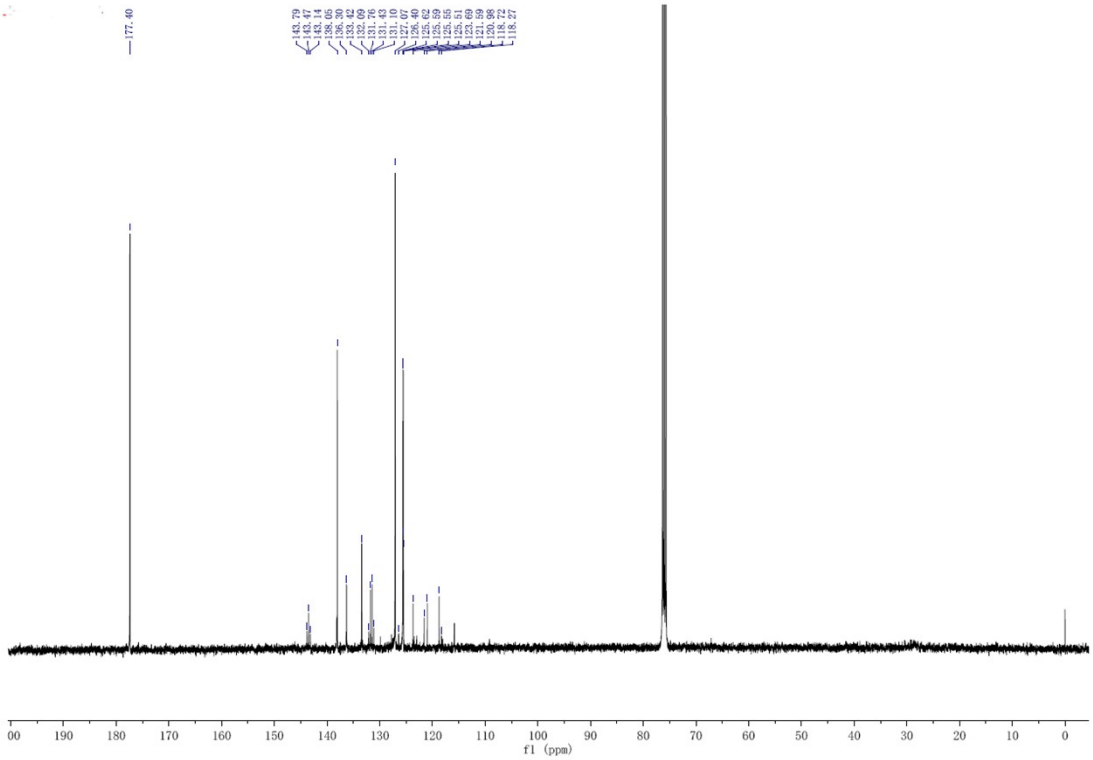
160.84
144.59
144.27
143.96
137.17
134.97
128.66
126.09
122.74
119.87
117.60
55.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.64
7.87
7.75
7.73
7.44
7.42
F
F
F
F
F
Cl
N
N
O
H
1.00
1.00
2.09
2.13
f1 (ppm)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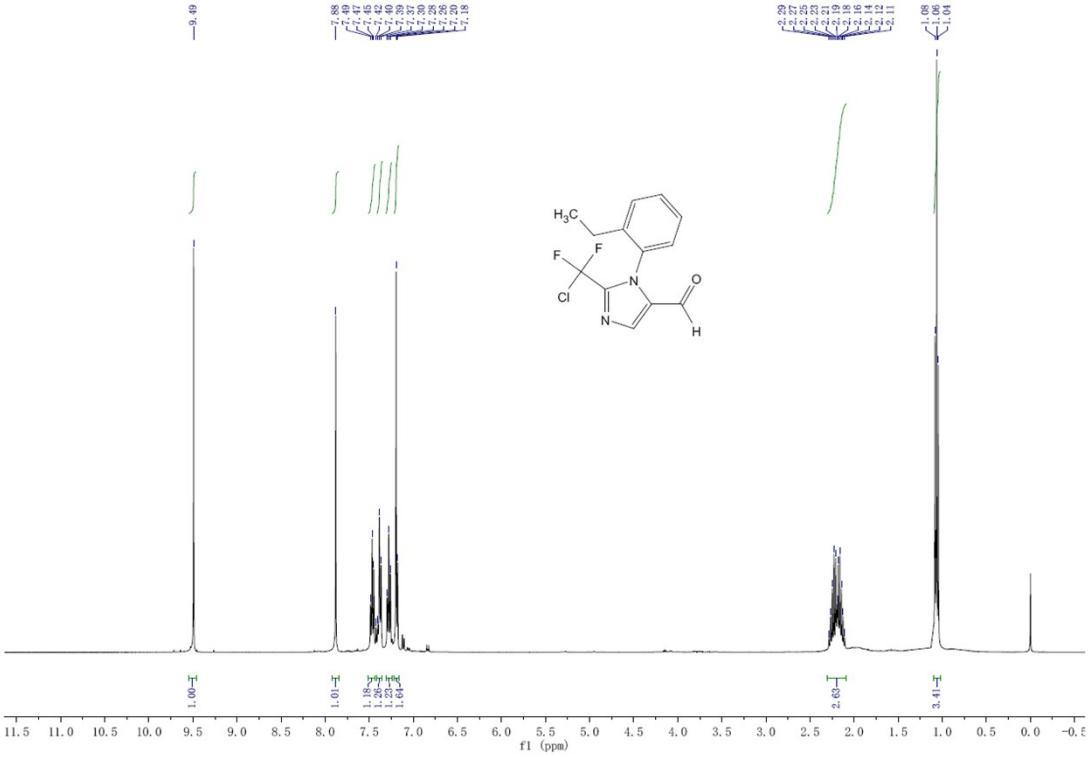
143.79
143.47
143.14
138.65
136.39
133.42
132.69
131.76
131.43
131.10
127.07
126.40
125.92
125.59
125.55
125.51
123.69
121.39
120.98
118.72
118.27
f1 (ppm)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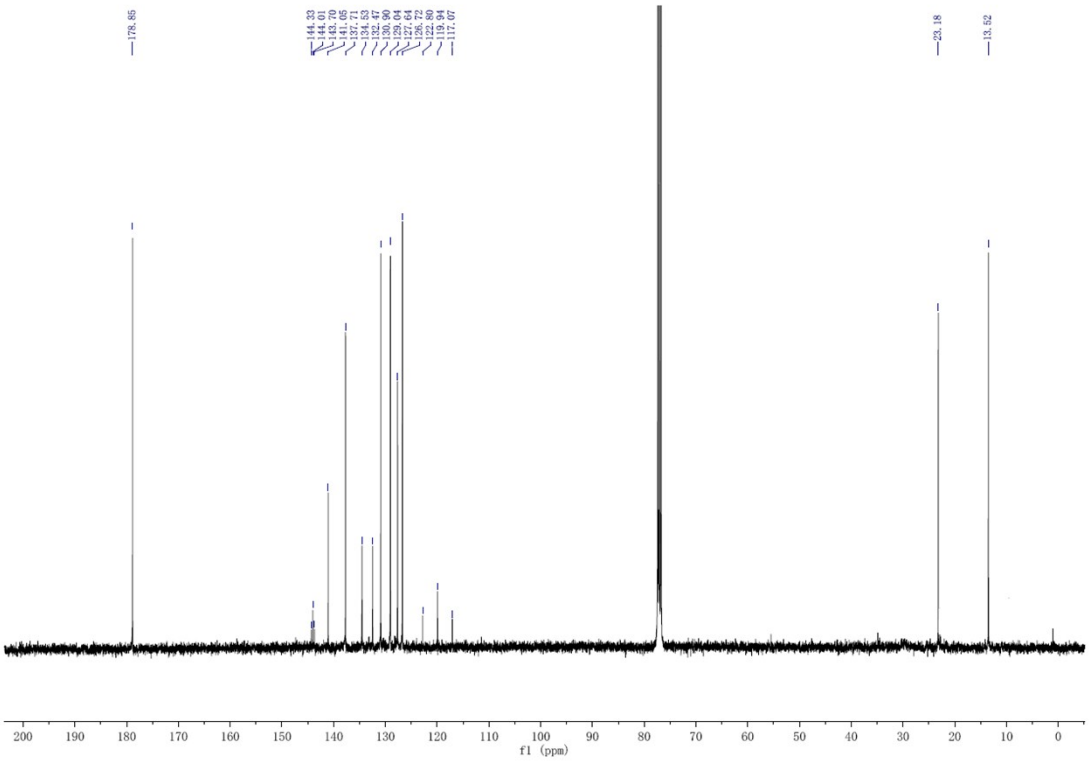
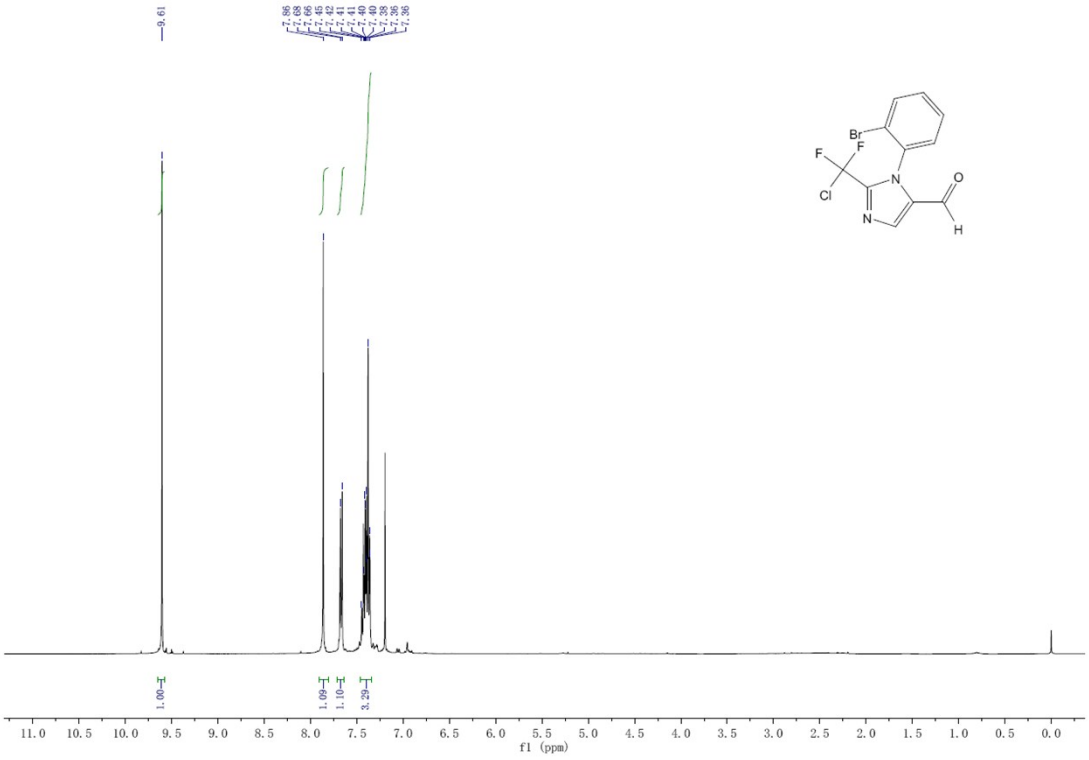
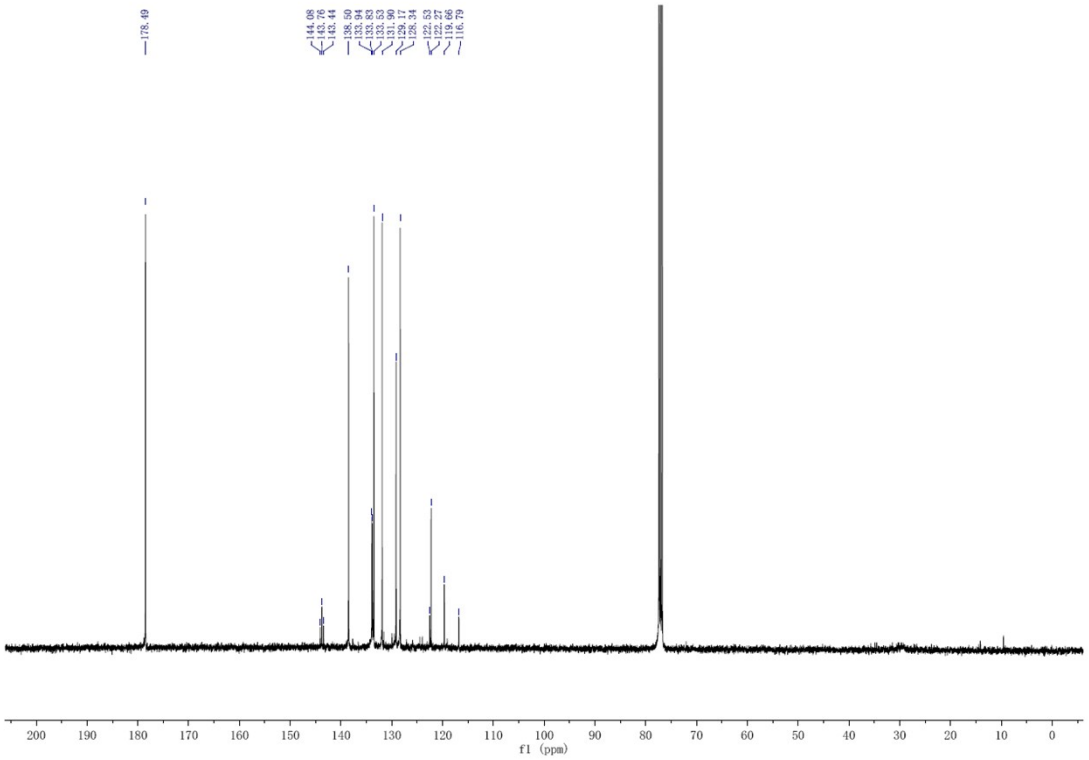
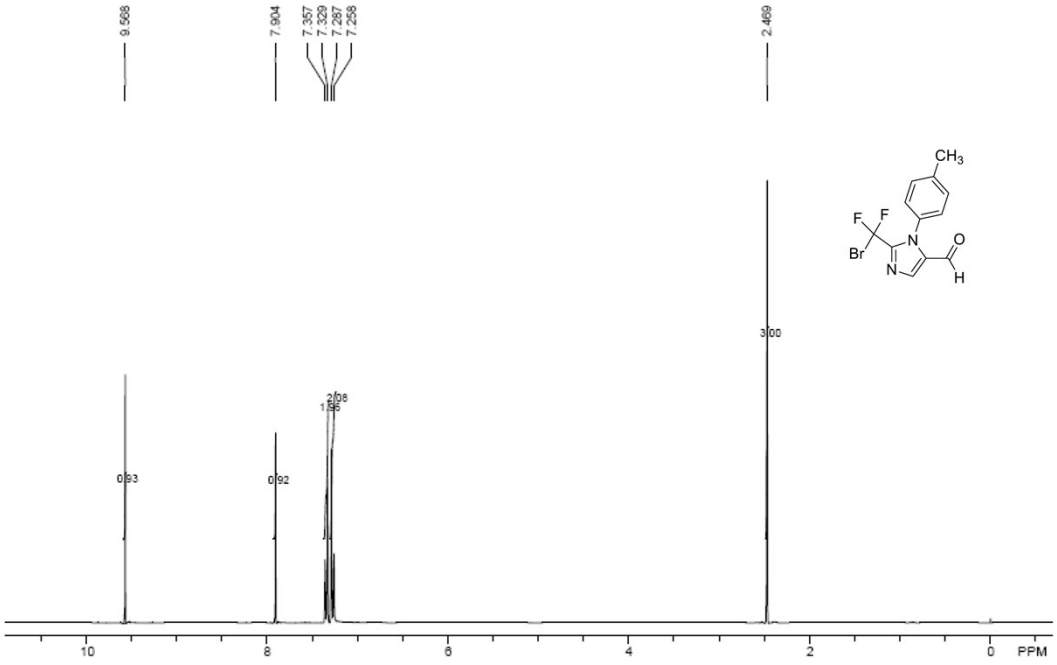
7.49
7.47
7.45
7.42
7.40
7.39
7.37
7.30
7.28
7.20
7.18
2.29
2.27
2.25
2.23
2.21
2.19
2.18
2.16
2.14
2.12
2.11
1.08
1.06
1.04
H3C
F
F
Cl
N
N
O
H
1.00
1.01
1.18
1.26
1.23
1.64
2.63
3.41
f1 (ppm)


178.85
144.33
144.01
143.70
141.05
137.71
136.53
132.47
130.90
129.04
127.64
126.72
122.80
119.94
117.07
23.18
13.52
f1 (ppm)


9.61
7.86
7.68
7.66
7.45
7.42
7.41
7.41
7.40
7.40
7.38
7.35
7.35
Br
F
F
F
Cl
N
N
O
H
1.00
1.09
1.10
3.29
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


178.49
144.08
143.76
143.44
138.50
133.94
133.83
133.53
131.90
129.17
128.34
122.53
122.27
119.46
116.79
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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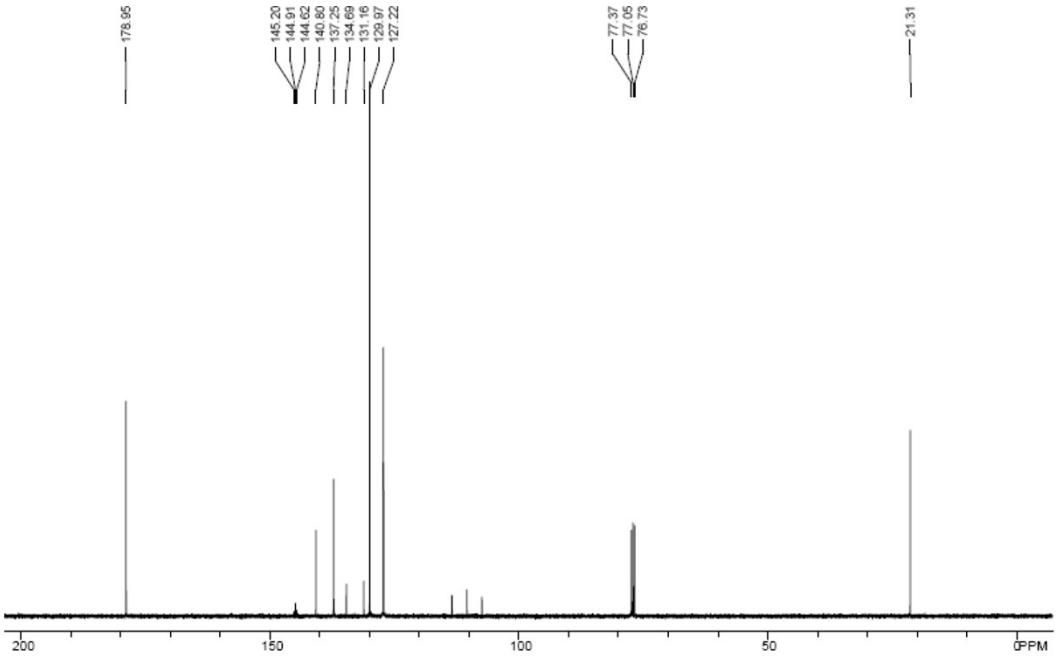
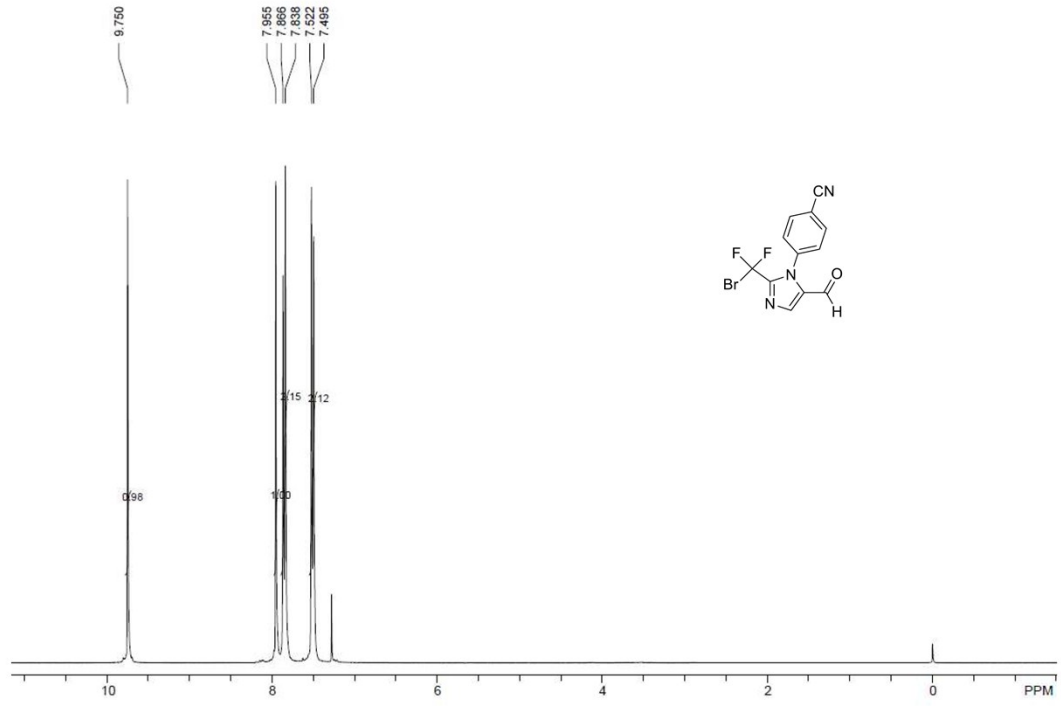
7.904
7.357
7.329
7.287
7.258
2.469
CH3
F
F
Br
N
N
O
H
3.00
2.06
1.95
0.93
0.92
10
8
6
4
2
0
PPM


178.95
145.20
144.91
144.62
140.80
137.25
134.69
131.16
129.97
127.22
77.37
77.05
76.73
21.31
200
150
100
50
0
PPM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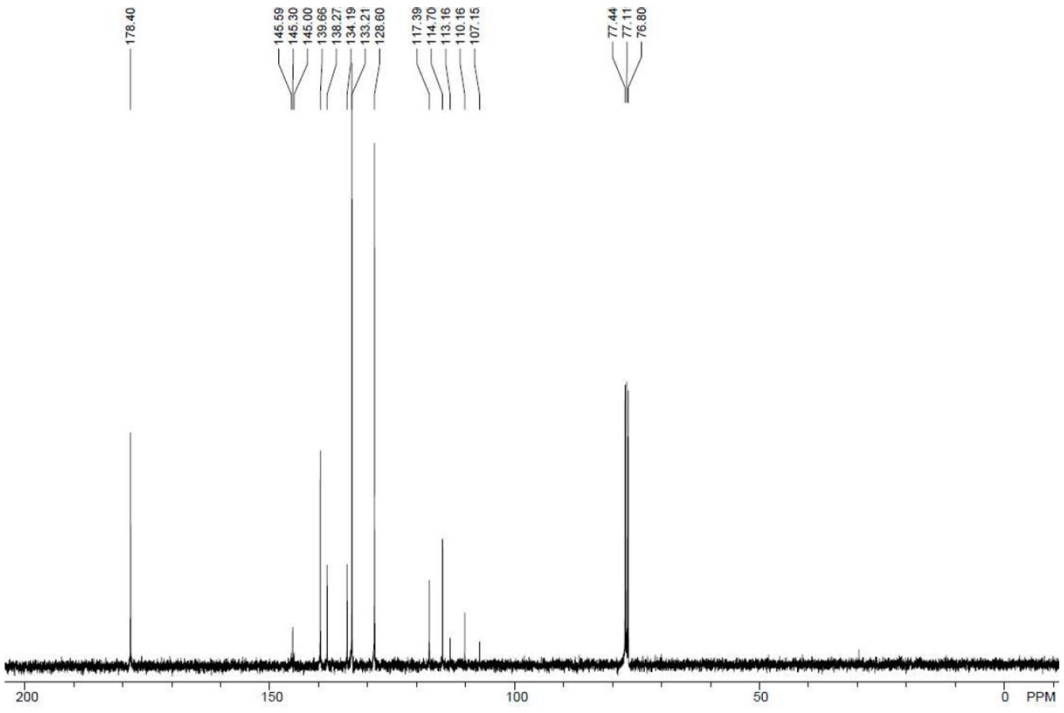
7.955
7.866
7.838
7.522
7.495
CN
F
F
Br
N
N
O
H
2.15
2.12
0.98
1.00
10
8
6
4
2
0
PPM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77.11
76.80
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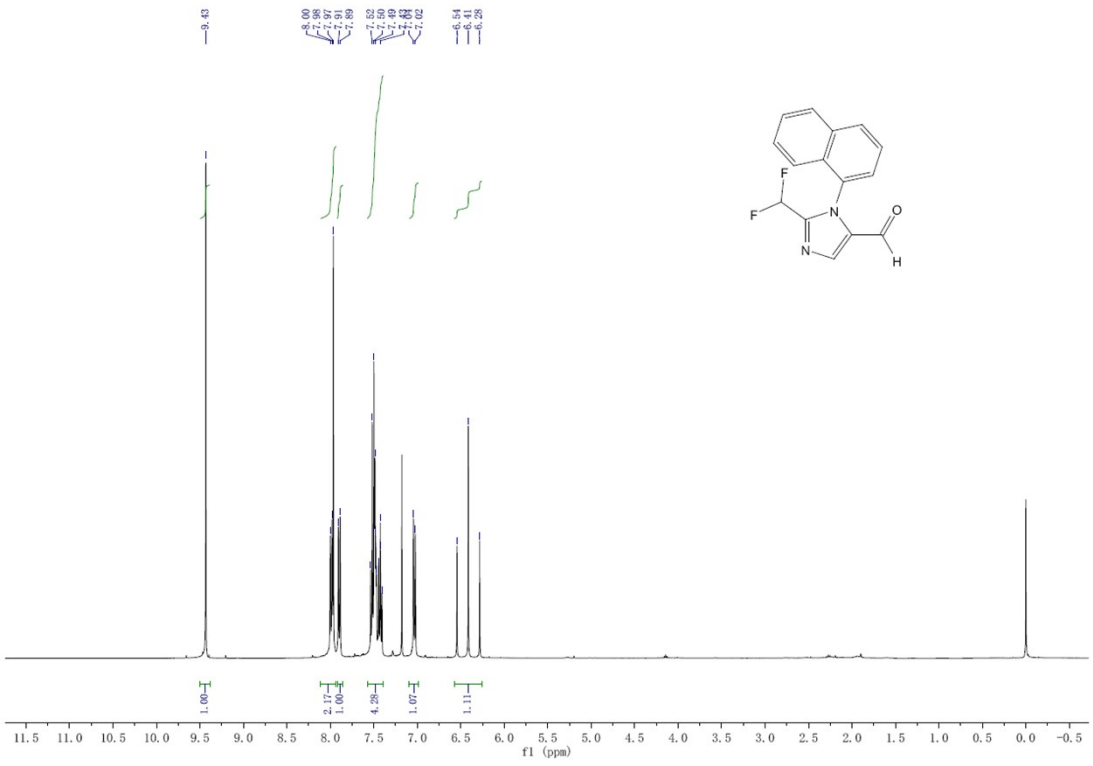
100
50
0
PPM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7.59
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7.02
6.54
6.41
6.25
F
F
N
O
N
H
1.00
2.17
1.00
4.28
1.07
1.11
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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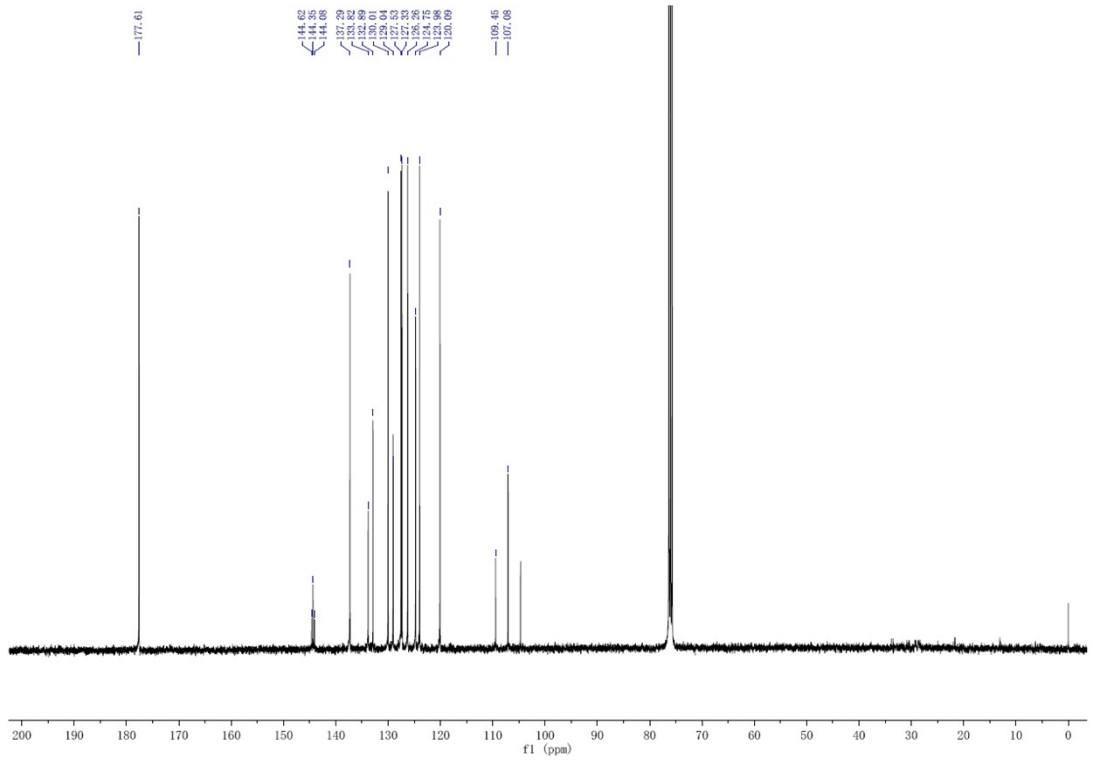
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127.33
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120.09
109.45
107.08
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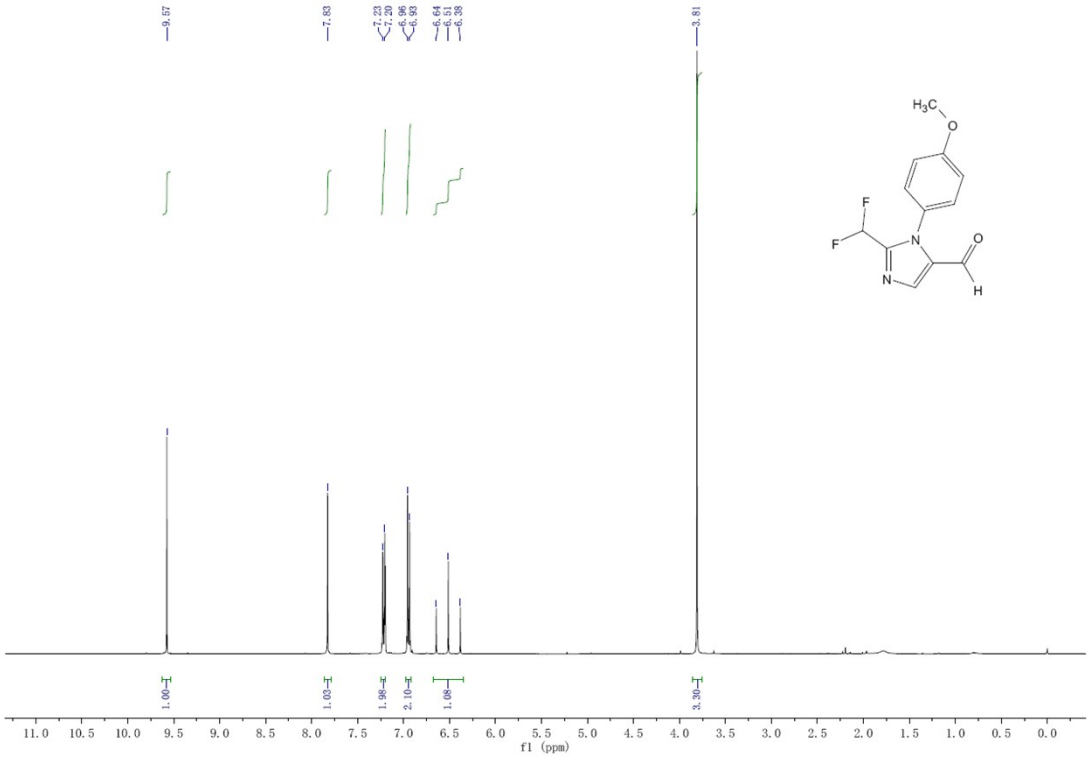
f1 (ppm)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1.03
1.98
2.10
1.08
3.30
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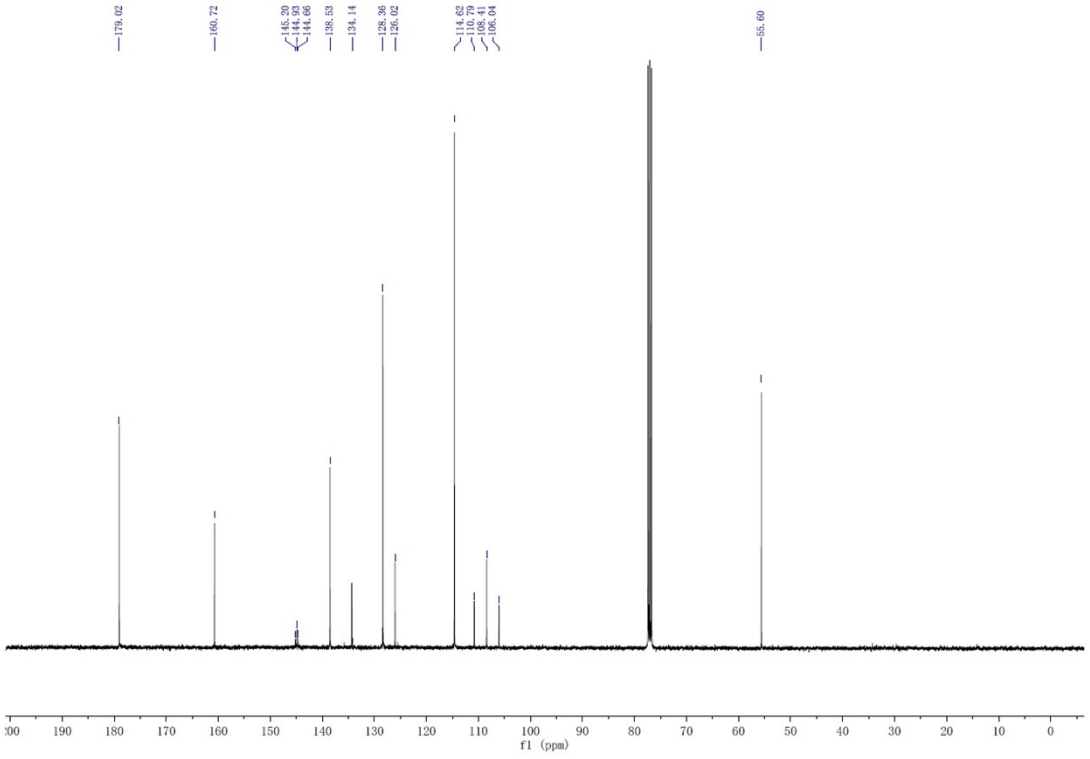
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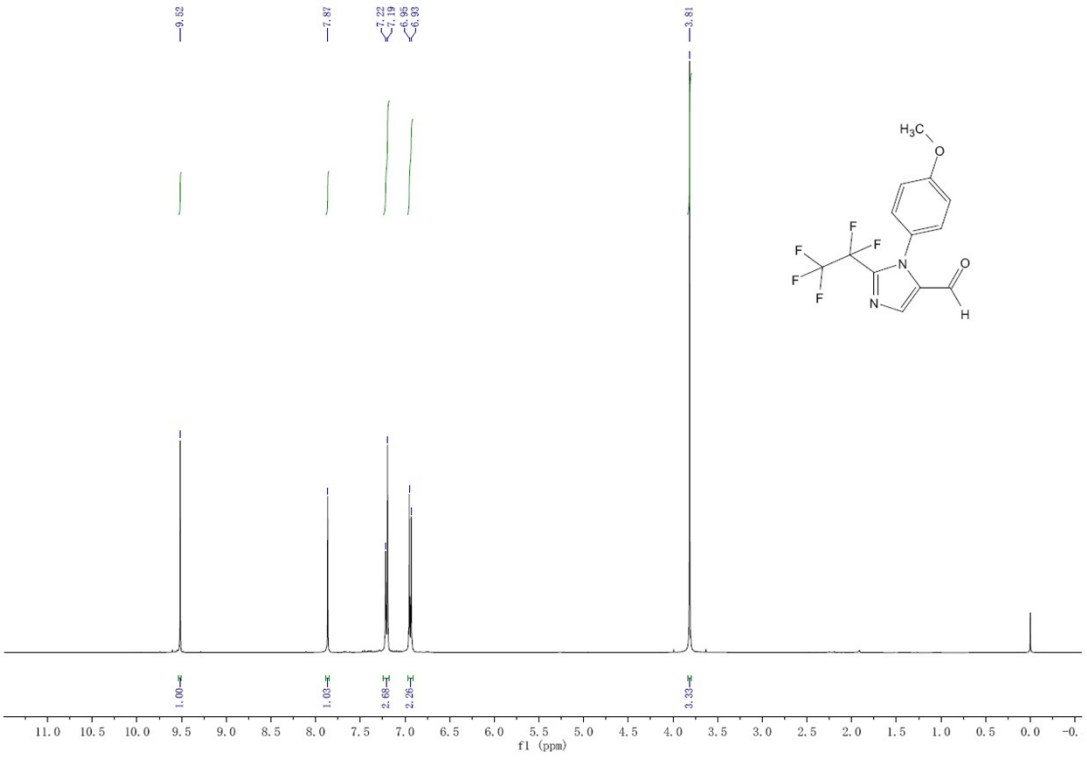
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1.00
1.03
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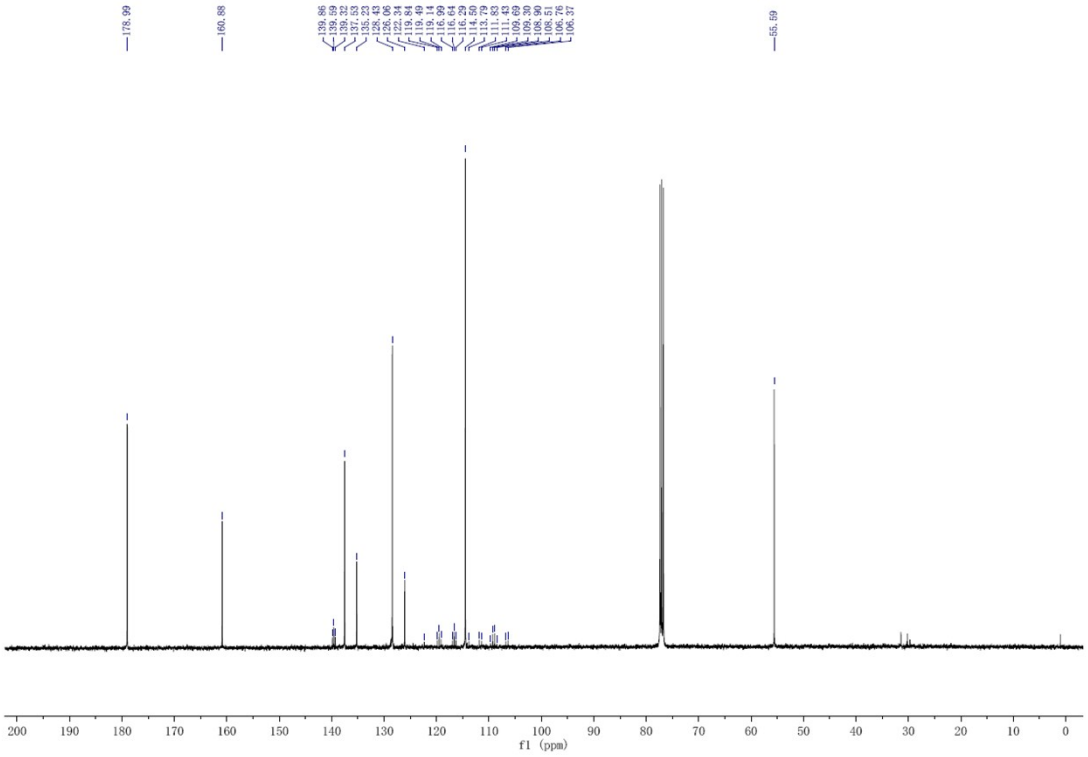
3.33
f1 (ppm)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116.29
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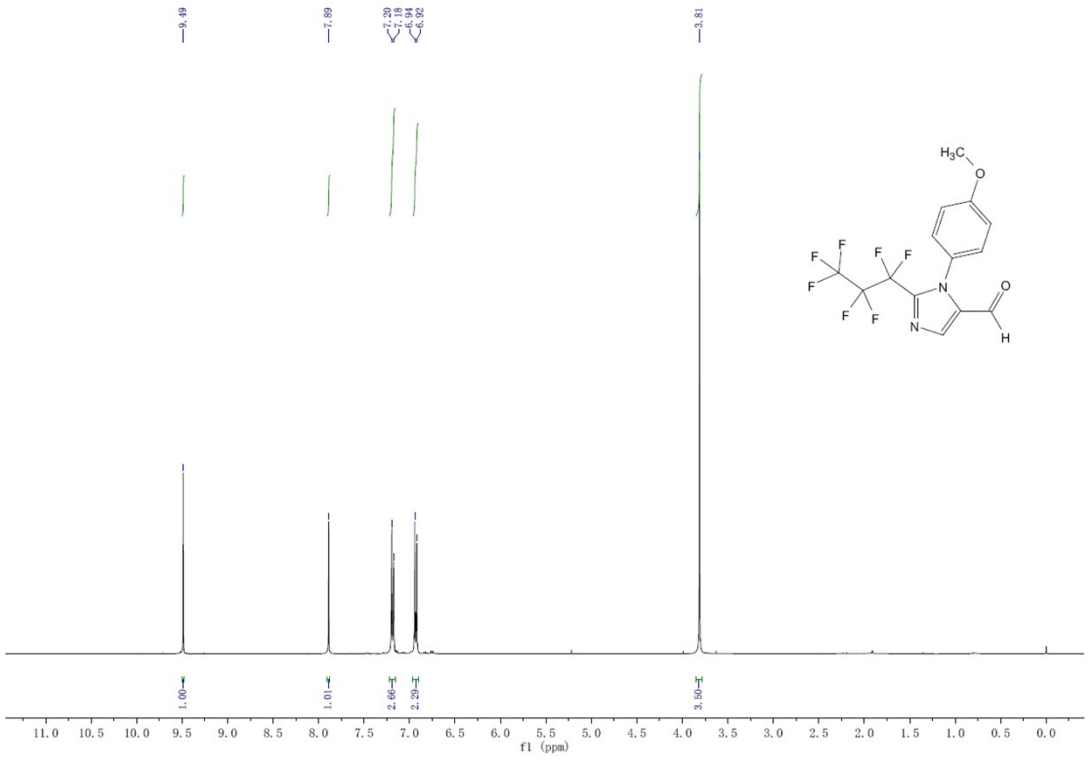
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7.20
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6.94
6.92
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1.00
1.01
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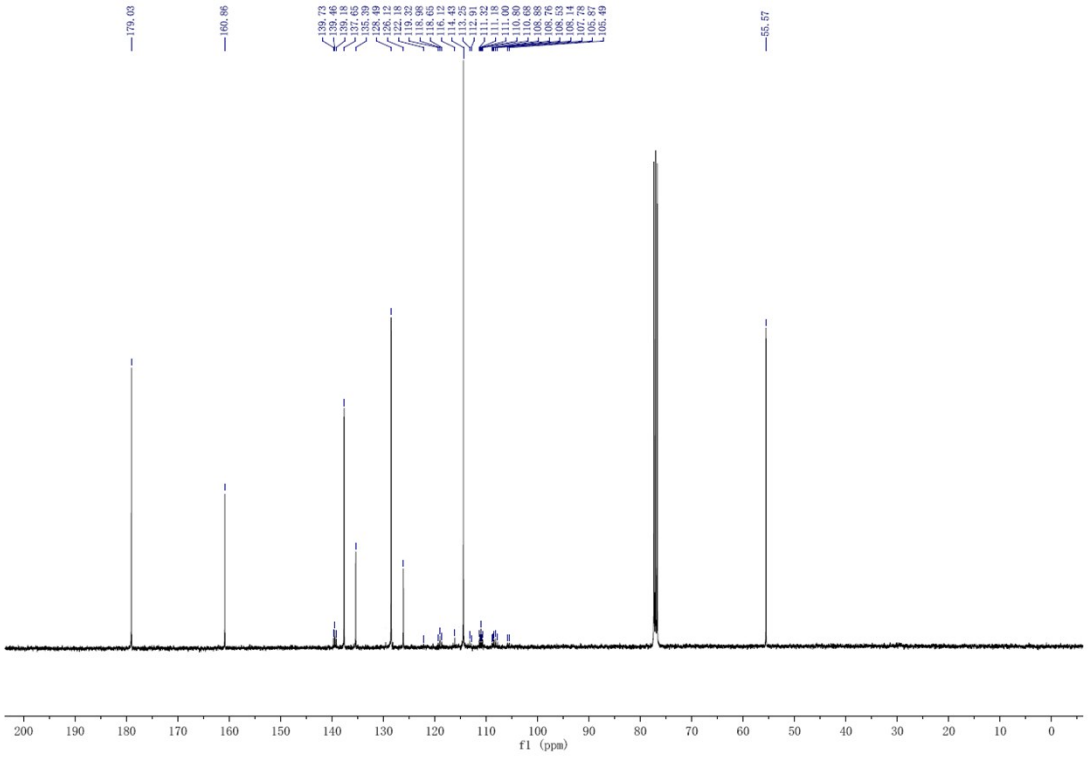
f1 (ppm)
H3C
O
F
F
F
F
F
F
N
N
O
H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119.32
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118.65
116.12
114.43
113.25
112.91
111.32
111.18
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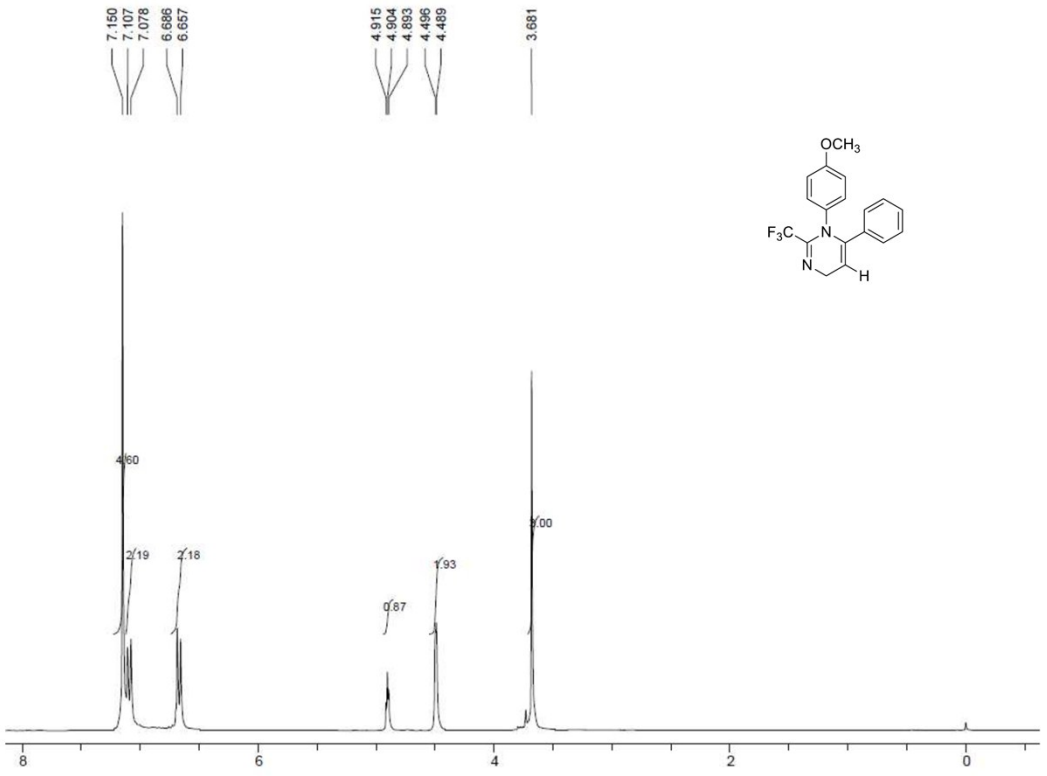
108.76
108.53
108.14
107.78
105.87
105.49
55.57
f1 (ppm)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6.657
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4.893
4.496
4.489
3.681
OCH3
F3C
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N
H
4.60
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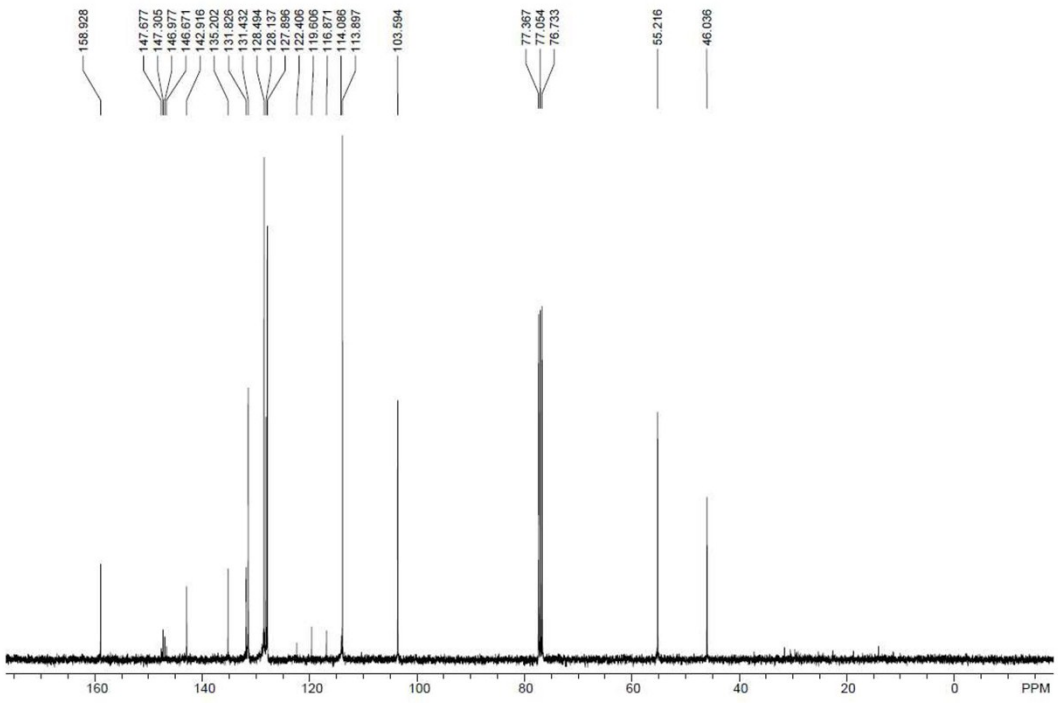
2.18
0.87
1.93
3.00
8
6
4
2
0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131.432
128.494
128.137
127.896
122.406
119.606
116.871
114.086
113.897
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76.733
55.216
46.036
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120
100
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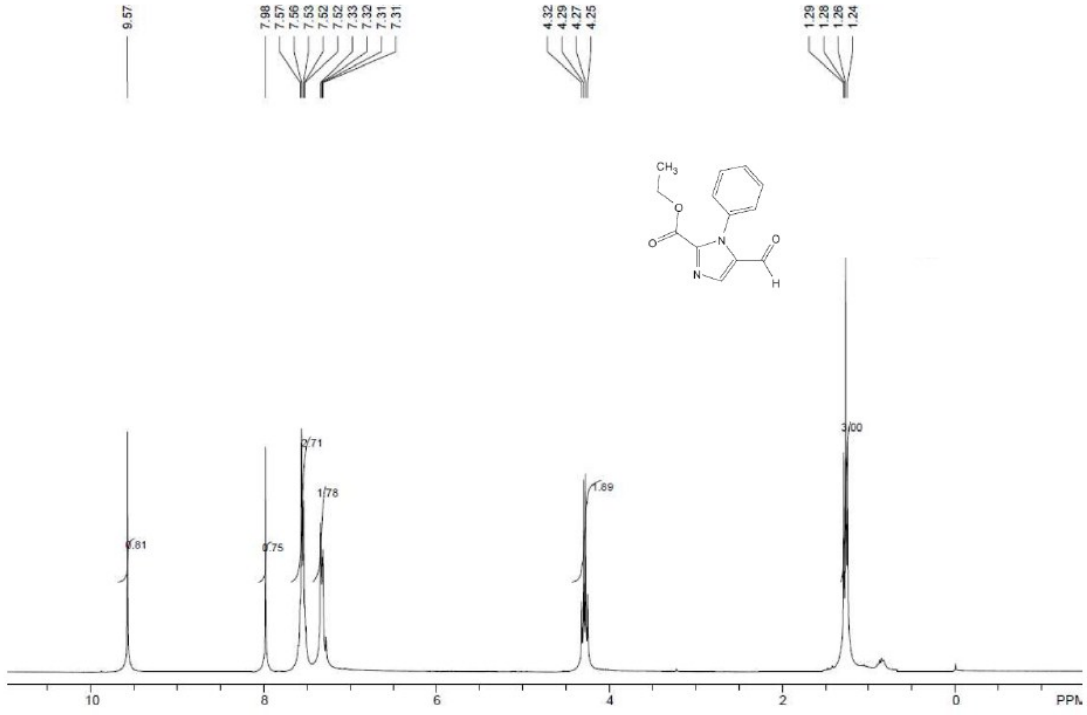
60
40
20
0
PPM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7.31
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4.32
4.29
4.27
4.25
1.29
1.28
1.26
1.24
CH3
O
O
N
N
O
H
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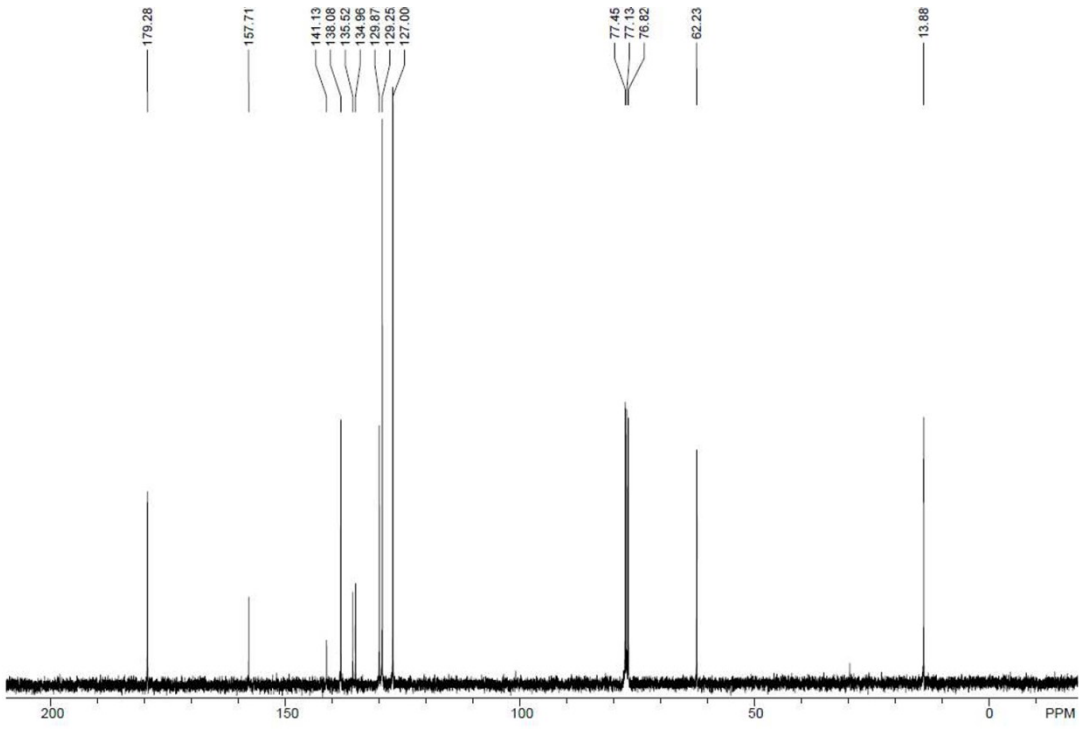
0.75
2.71
1.78
1.89
3.00
10
8
6
4
2
0
PPM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77.13
76.82
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13.88
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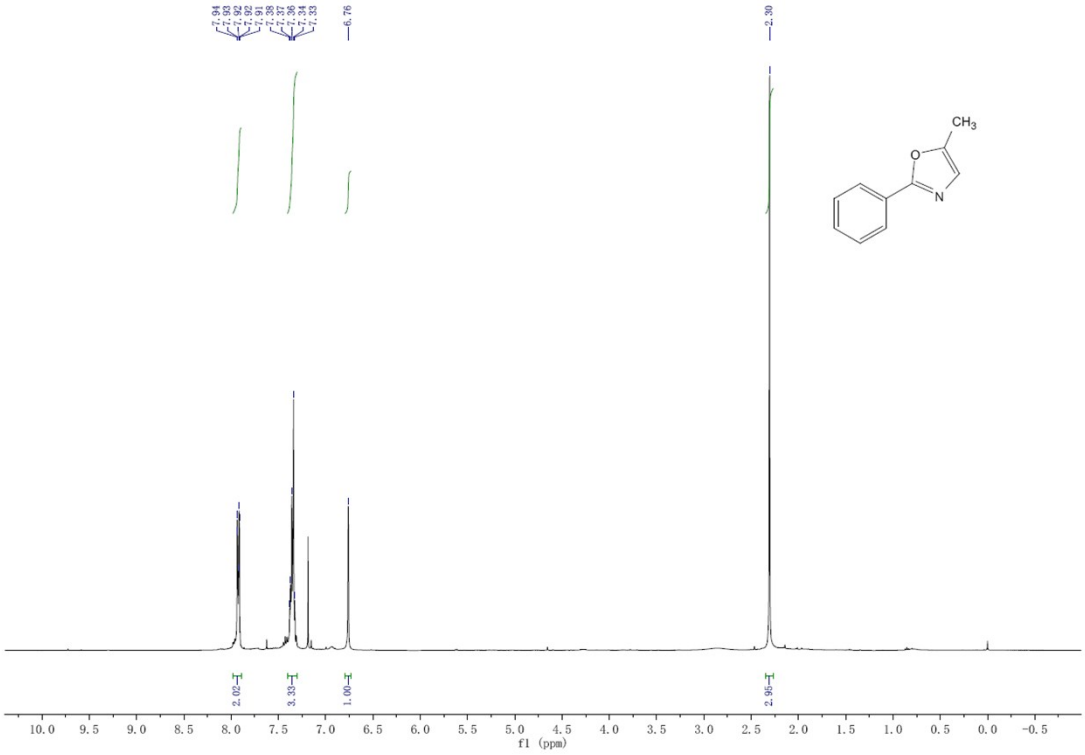
100
50
0
PPM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7.92
7.91
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6.76
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CH3
O
N
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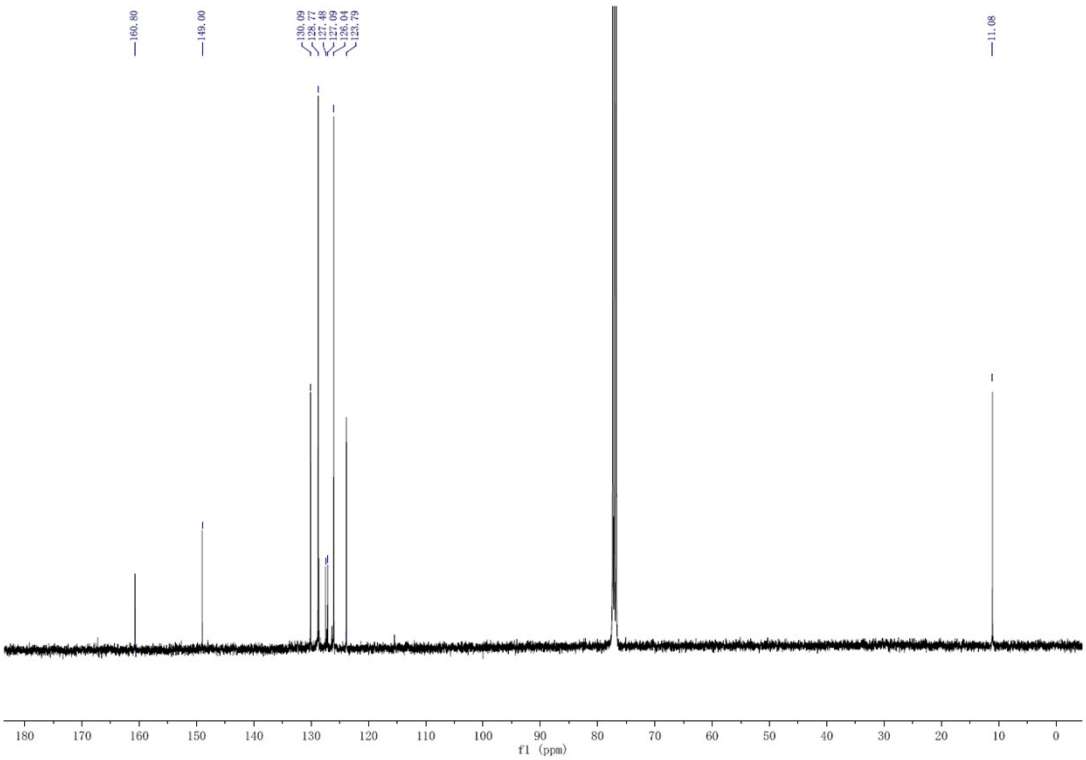
3.33
1.00
2.95
f1 (ppm)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127.09
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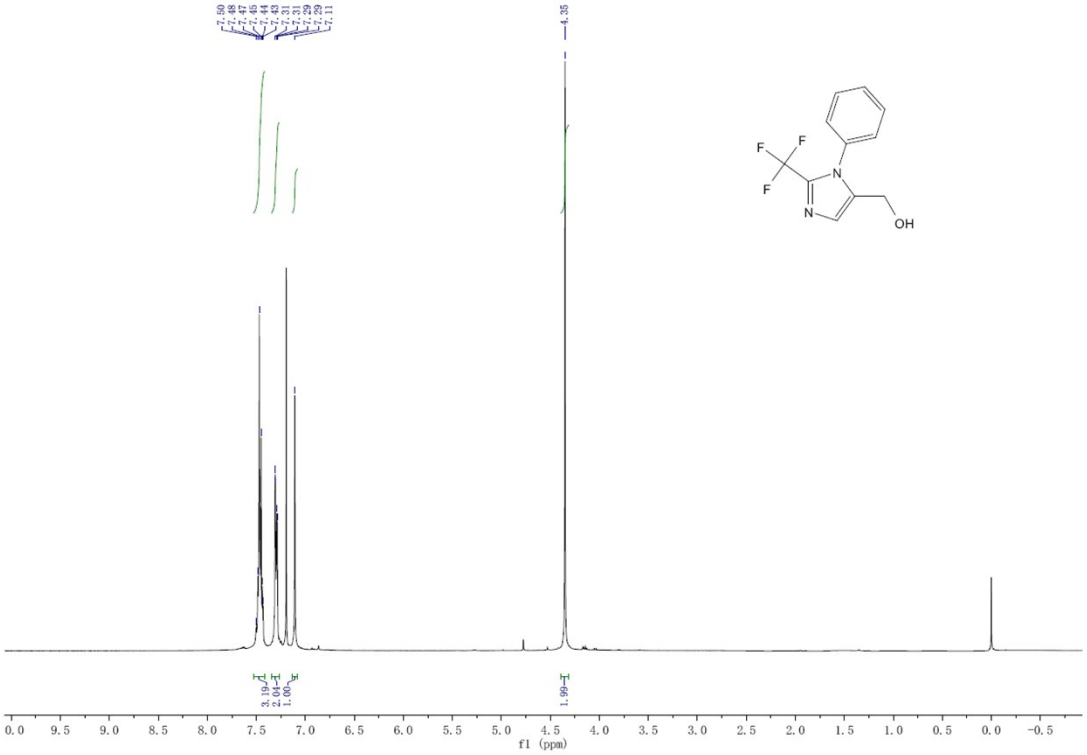
123.79
11.08
f1 (ppm)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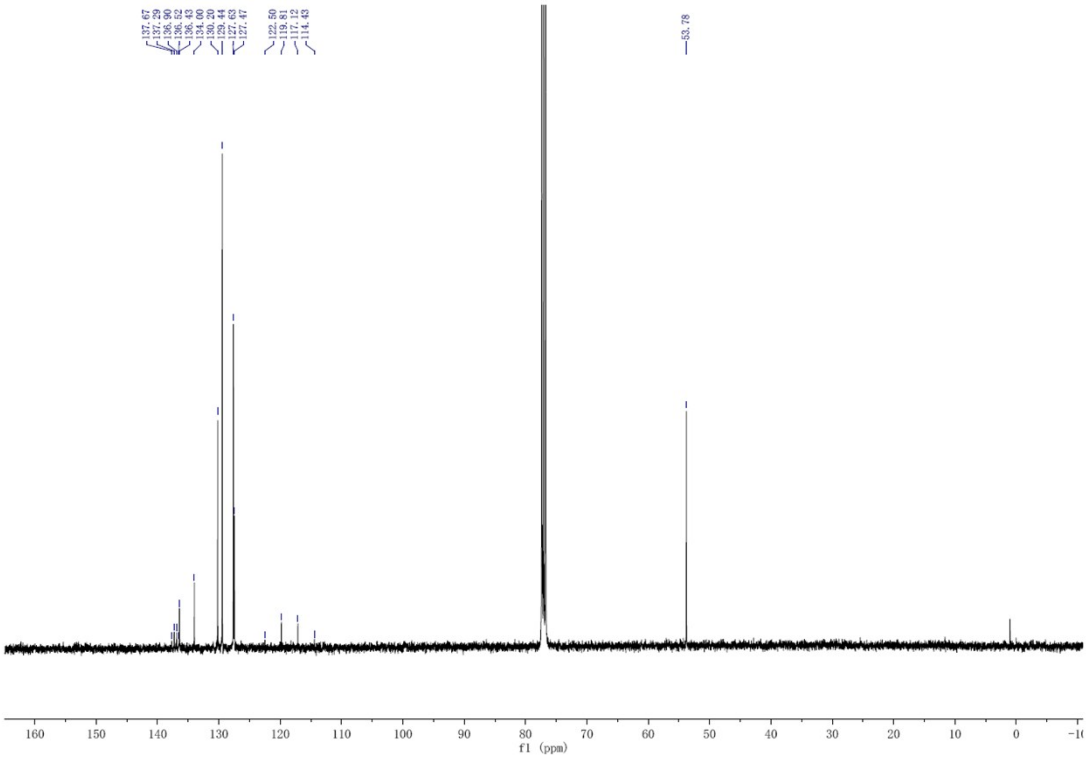
7.43
7.31
7.30
7.29
7.11
4.35
F
F
F
N
N
OH
3.10
2.04
1.00
1.99
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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129.44
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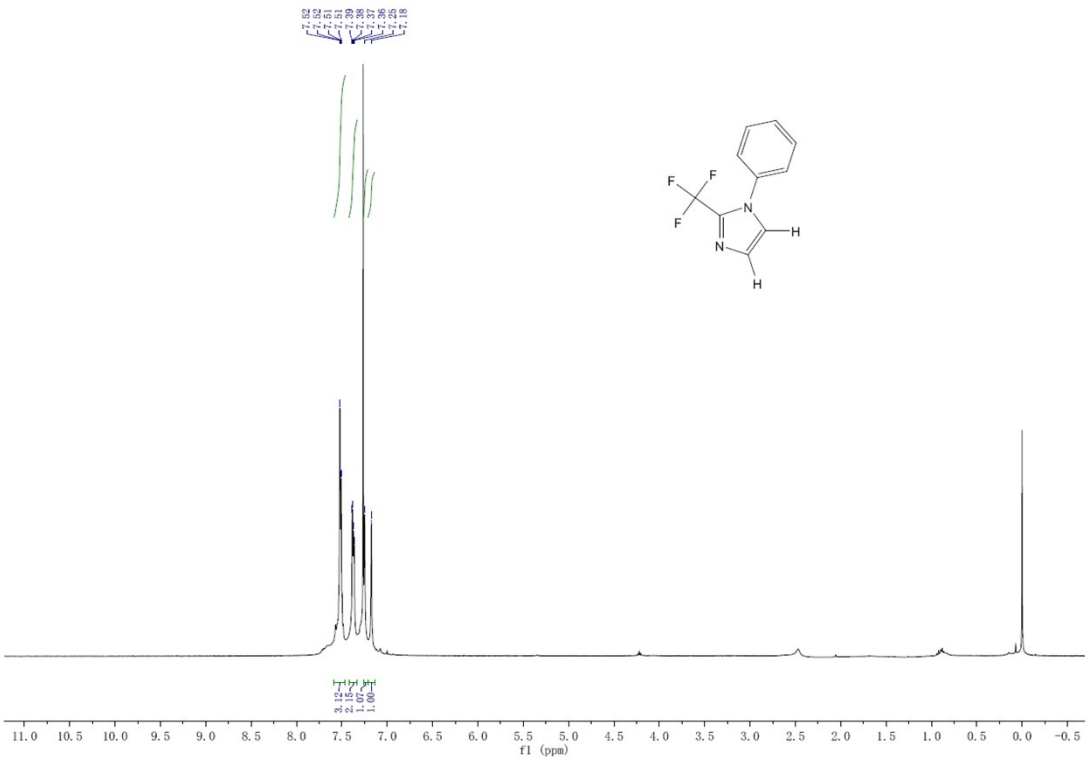
119.81
117.12
114.45
53.78
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.37
7.35
7.35
7.18
F
F
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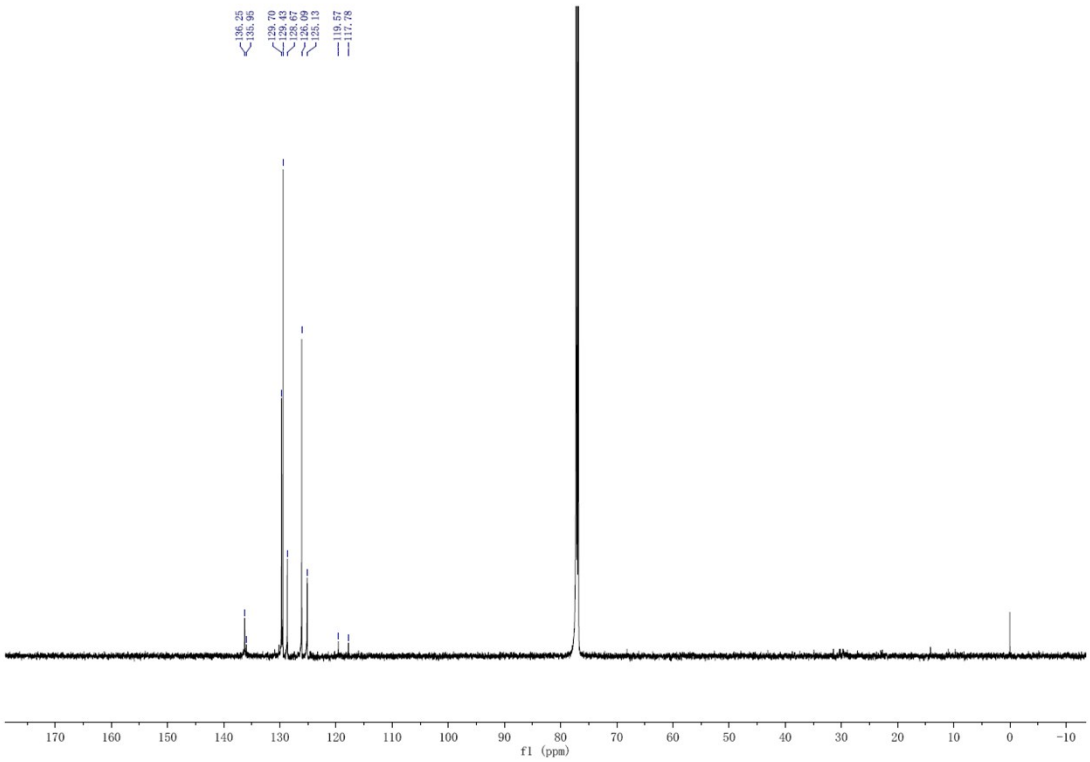
N
H
H
3.12
2.15
1.07
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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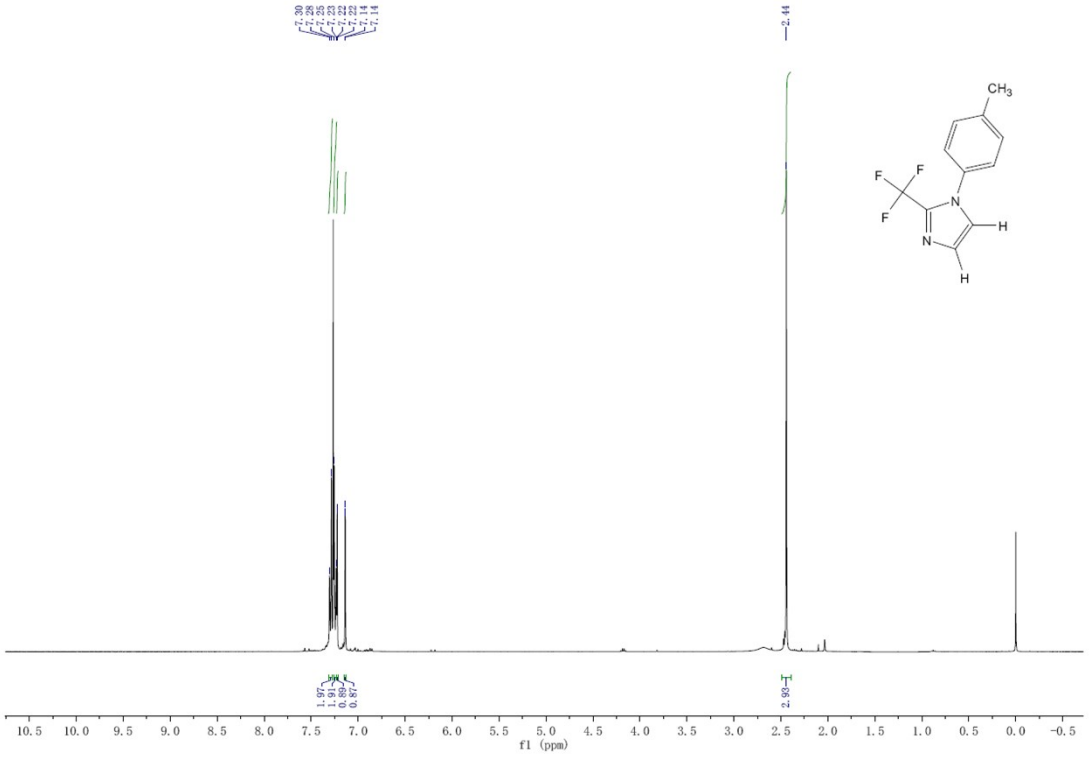
f1 (ppm)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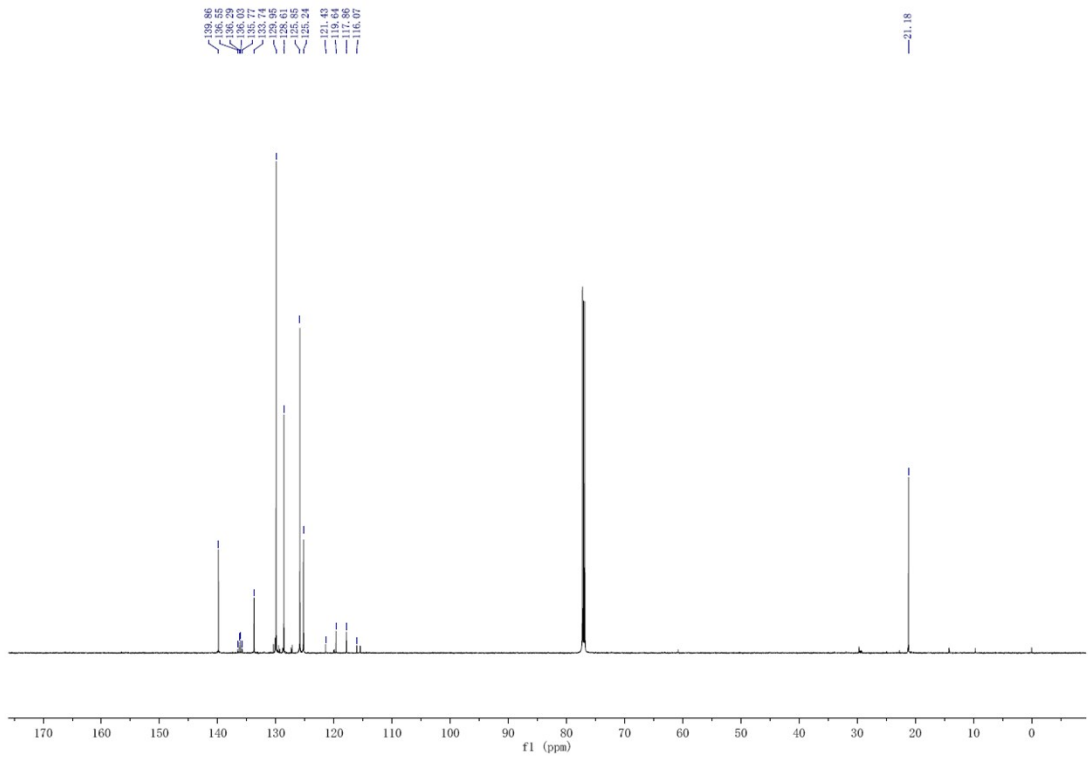
7.22
7.14
7.14
2.44
CH3
F
F
F
N
N
H
H
1.97
1.91
0.89
0.87
2.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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21.18
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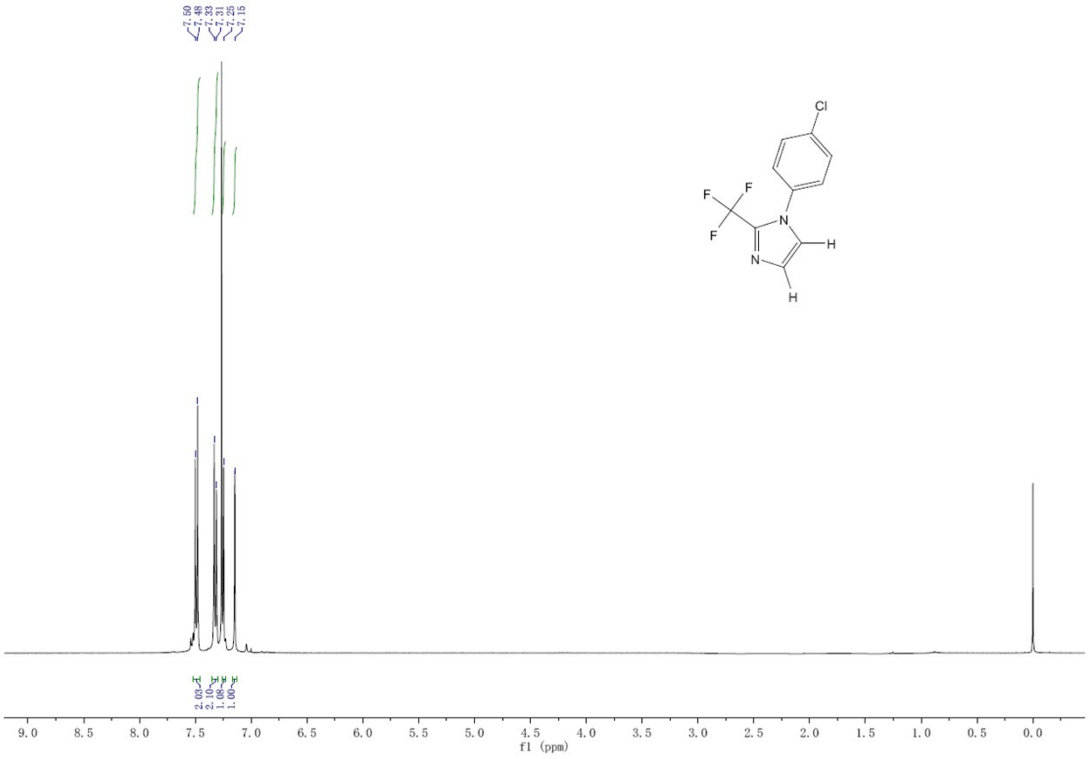
f1 (ppm)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7.25
7.15
2.03
2.10
1.08
1.00
Cl
F
F
F
N
N
H
H
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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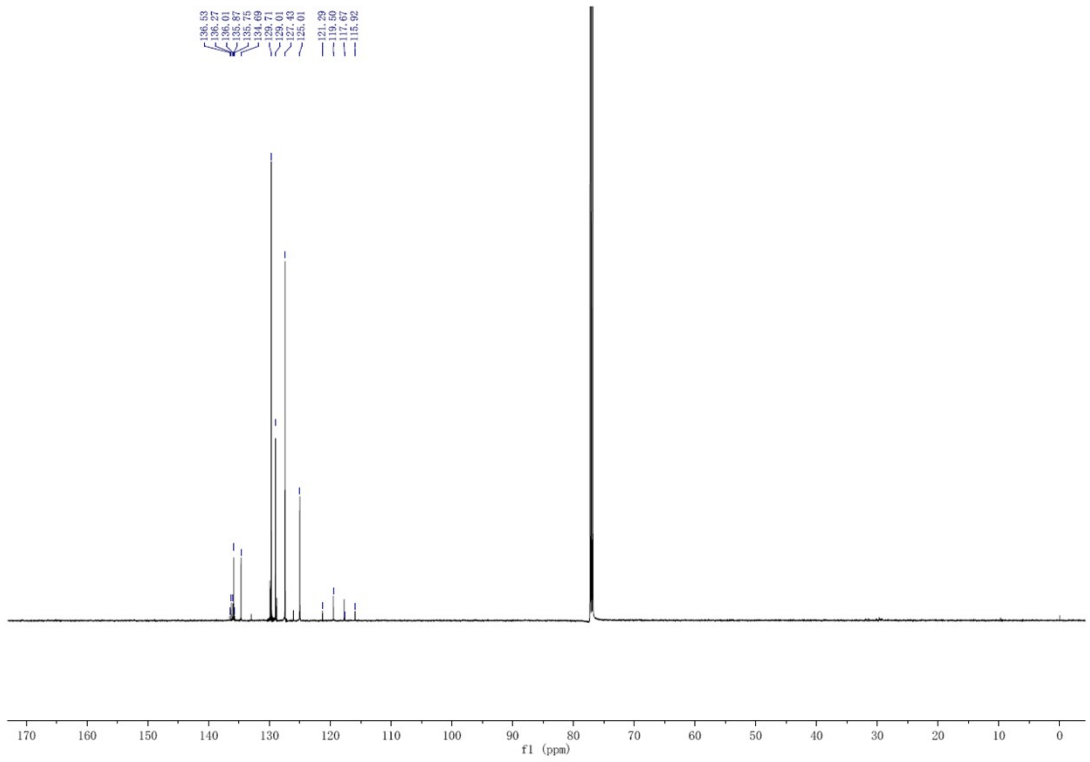
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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115.92
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130
120
110
100
90
80
70
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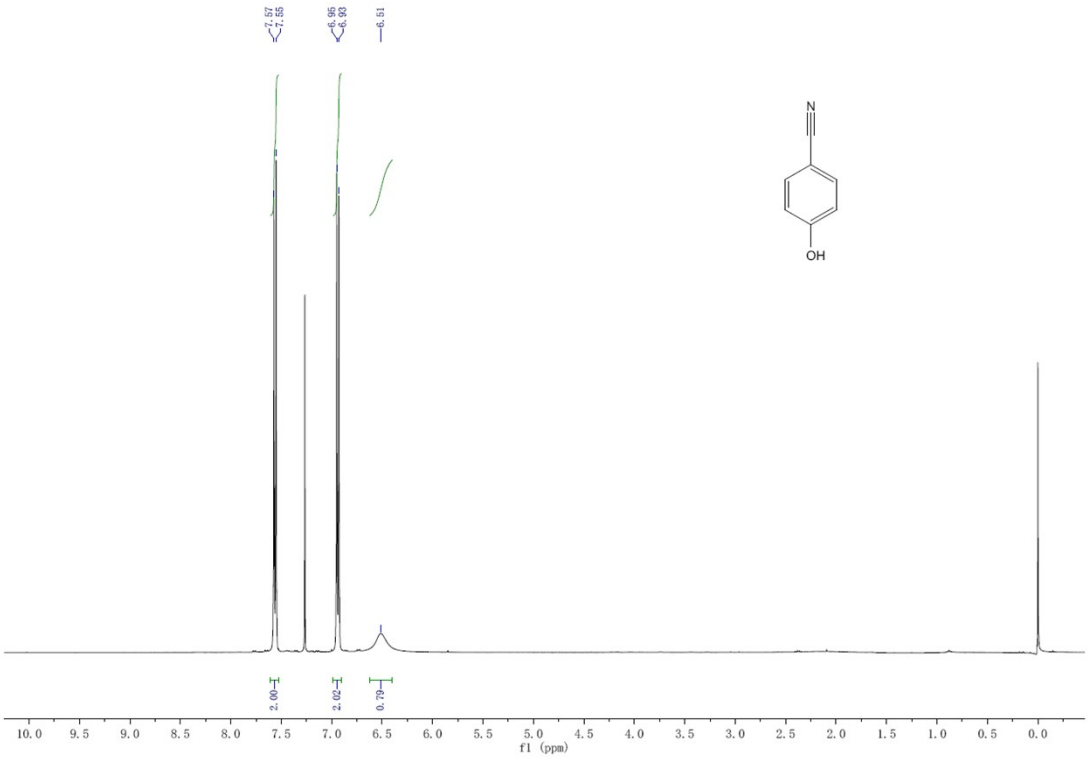
50
40
30
20
10
0
f1 (ppm)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7.55
6.96
6.93
6.51
N
OH
2.00
2.02
0.79
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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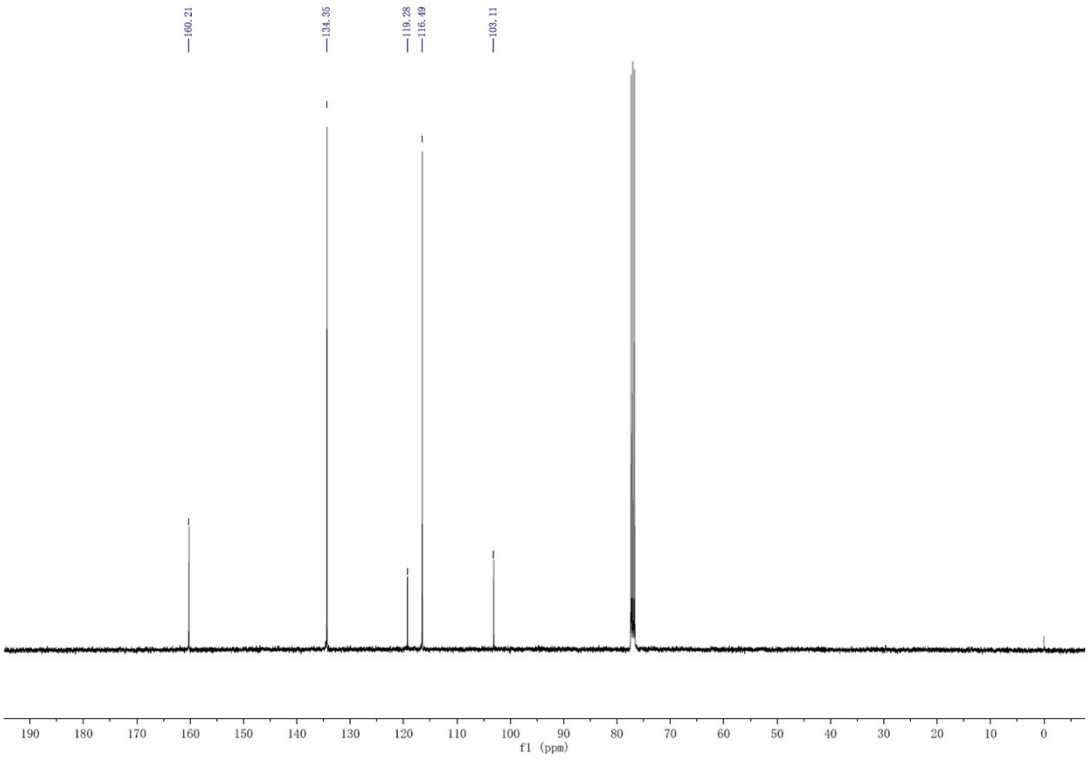
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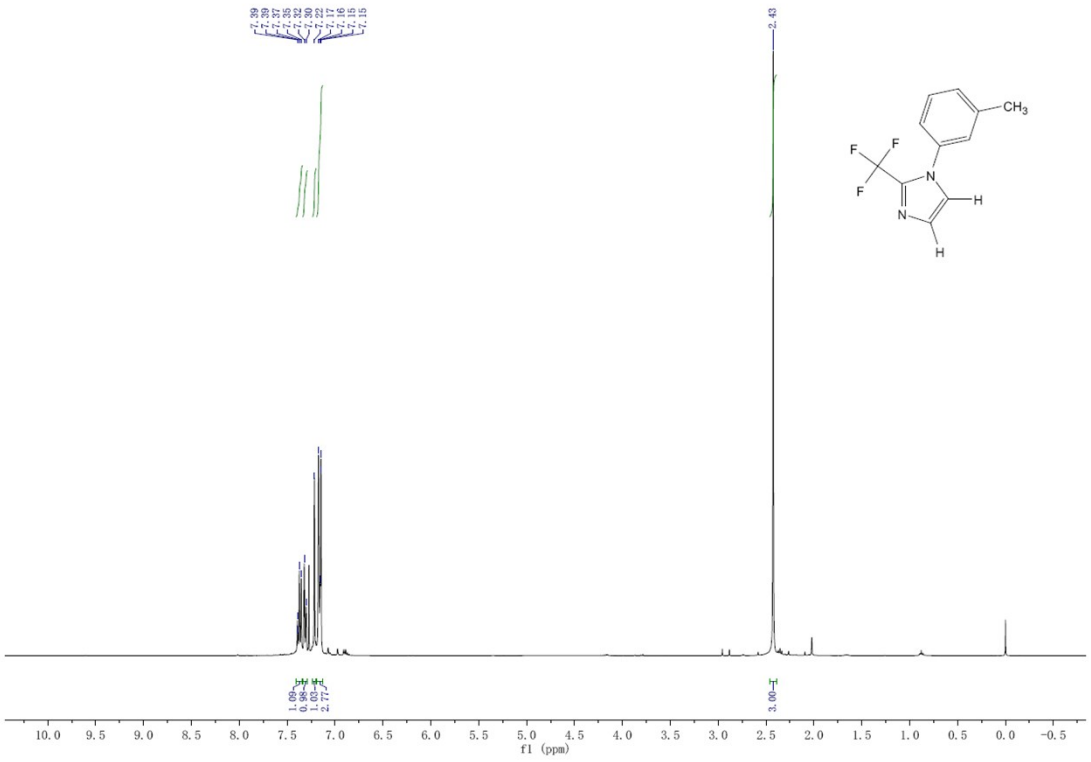
f1 (ppm)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7.17
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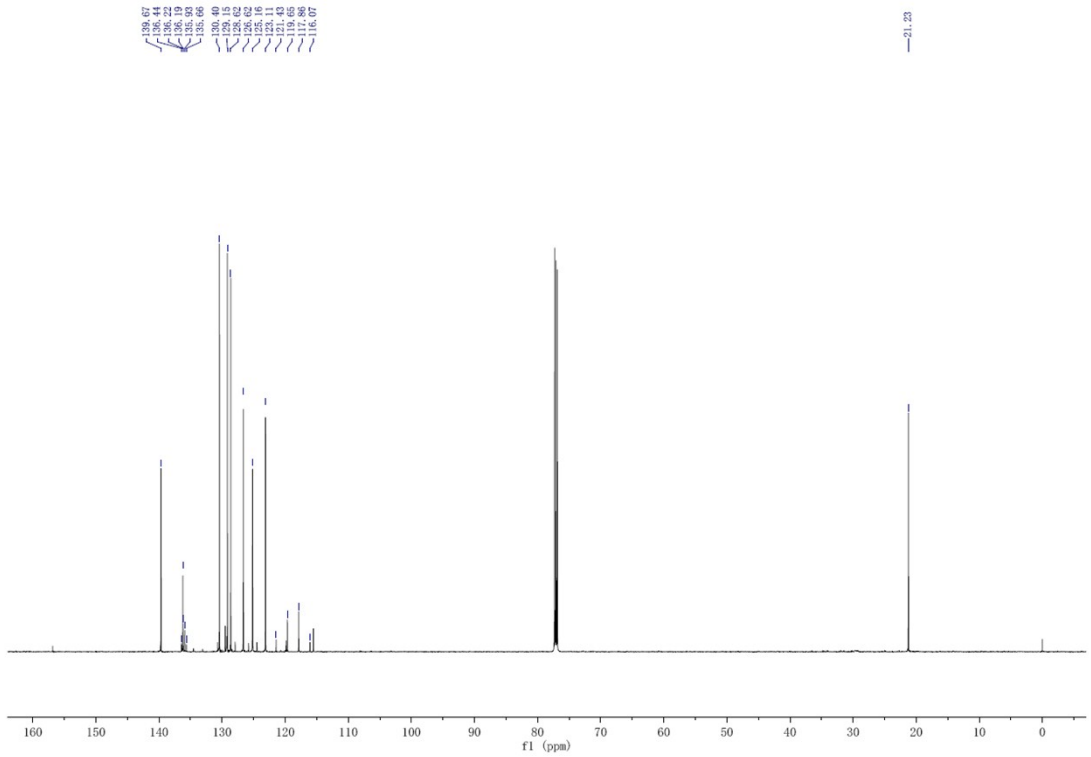
7.15
7.15
2.43
CH3
F
F
F
N
N
H
H
1.09
0.98
1.03
2.77
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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117.86
116.07
21.23
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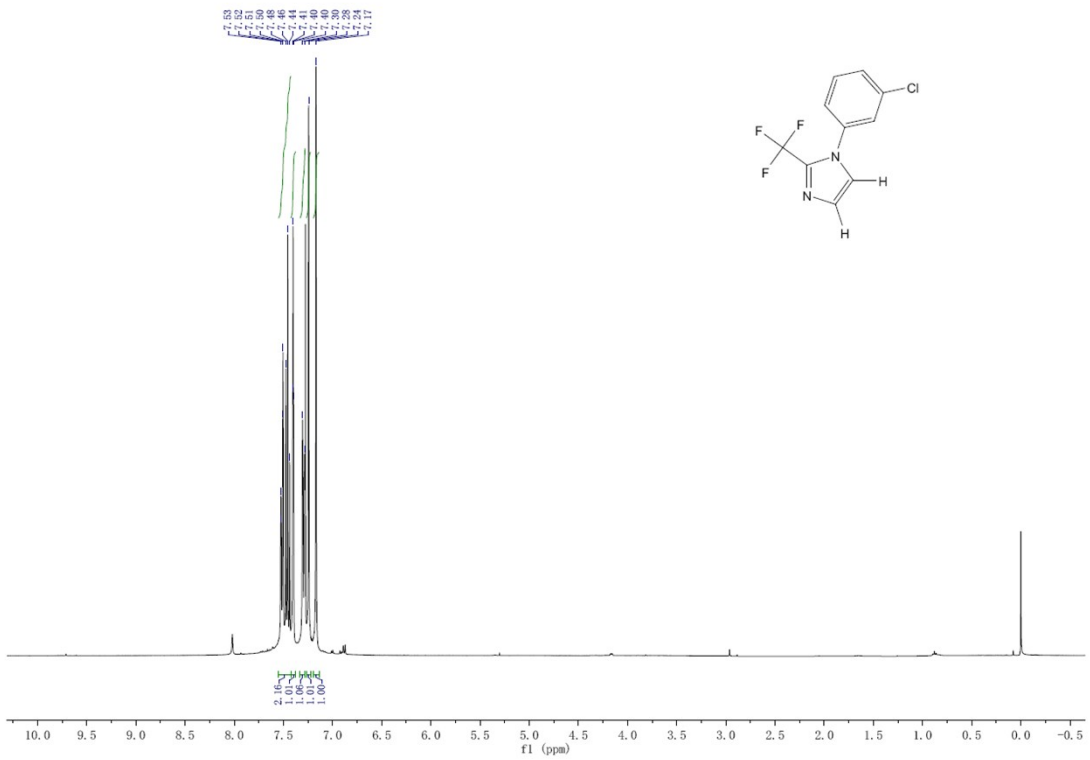
f1 (ppm)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7.24
7.17
Cl
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F
N
N
H
H
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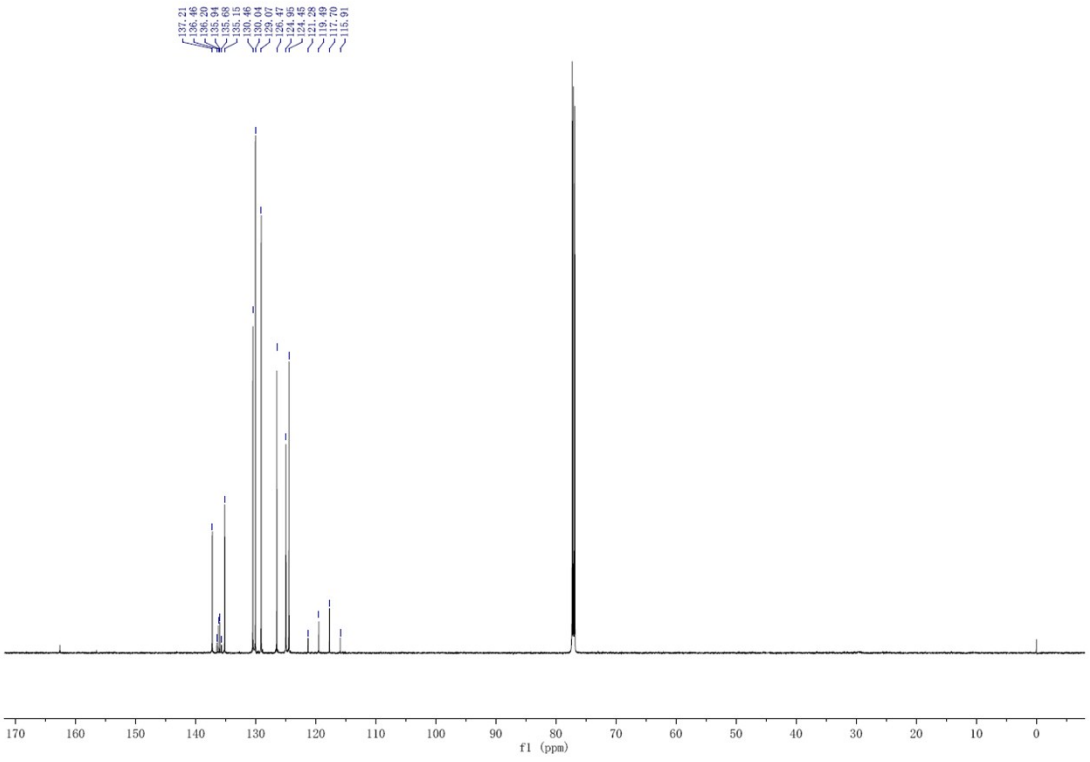
1.01
1.06
1.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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117.70
115.91
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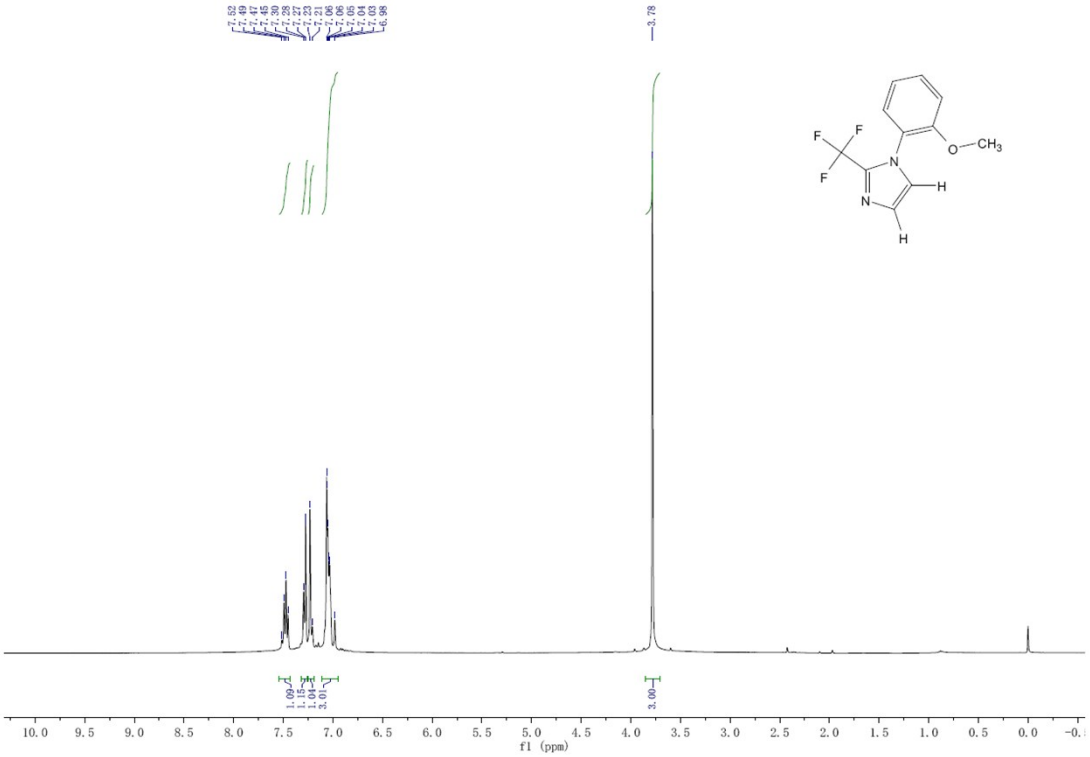
f1 (ppm)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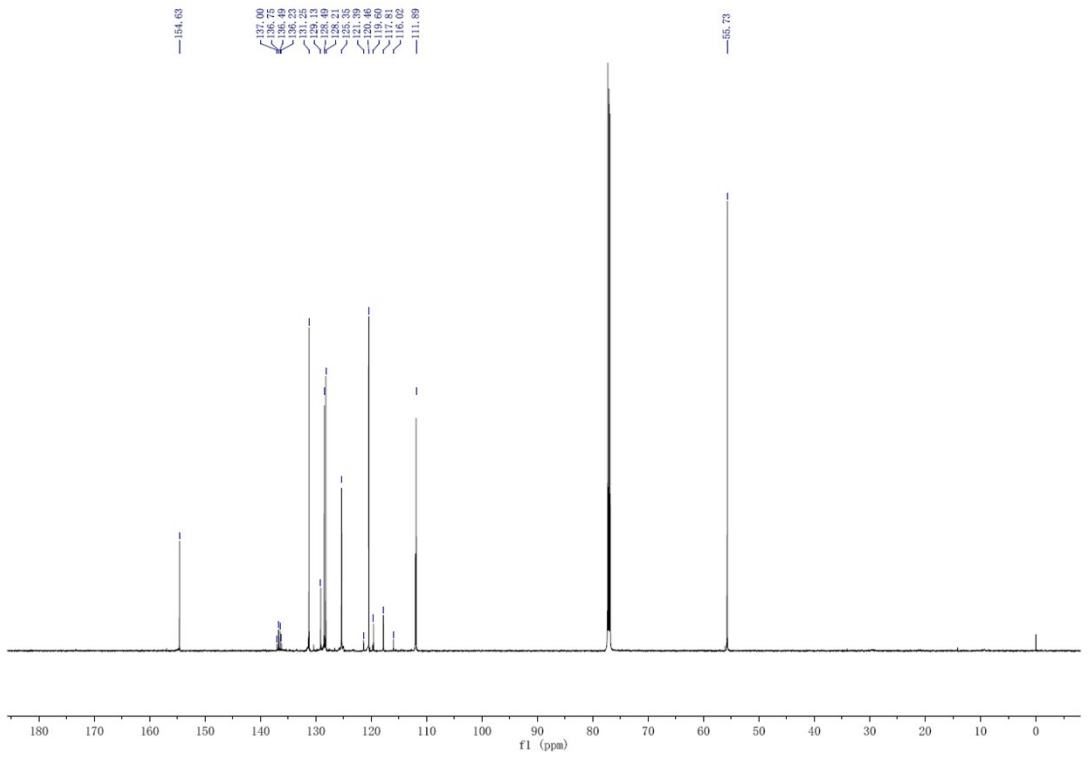
7.04
7.03
6.98
3.78
F
F
F
N
N
H
H
O
CH3
1.09
1.15
1.04
1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.21
125.35
121.39
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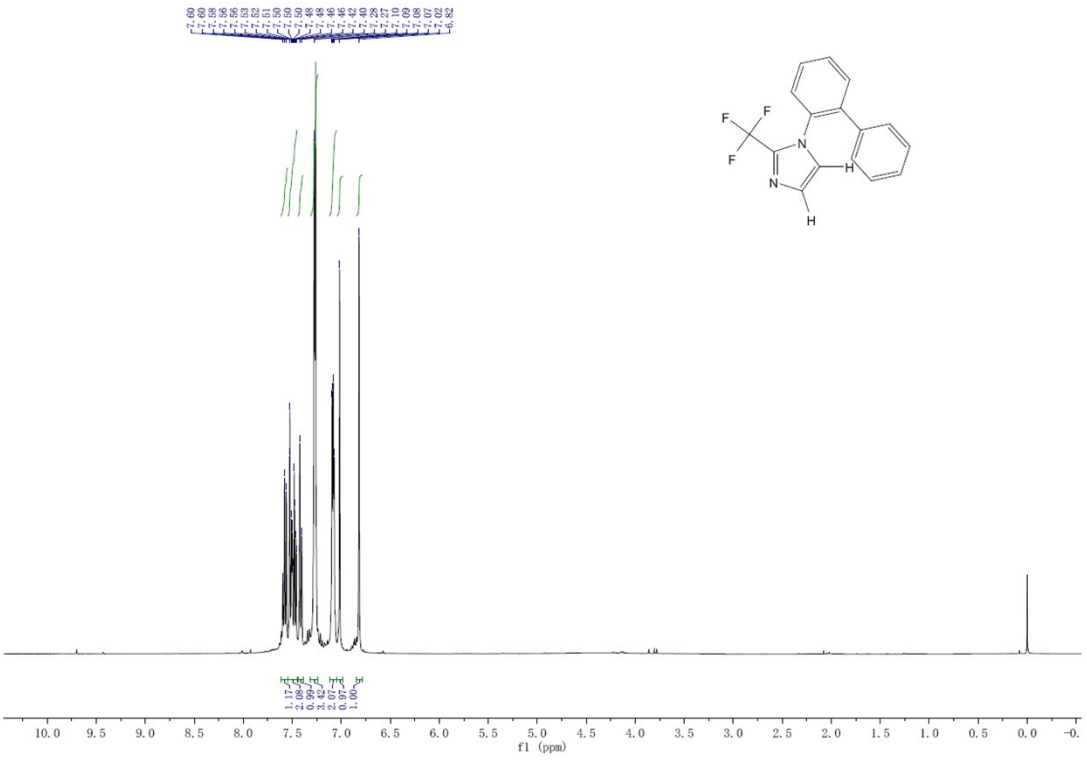
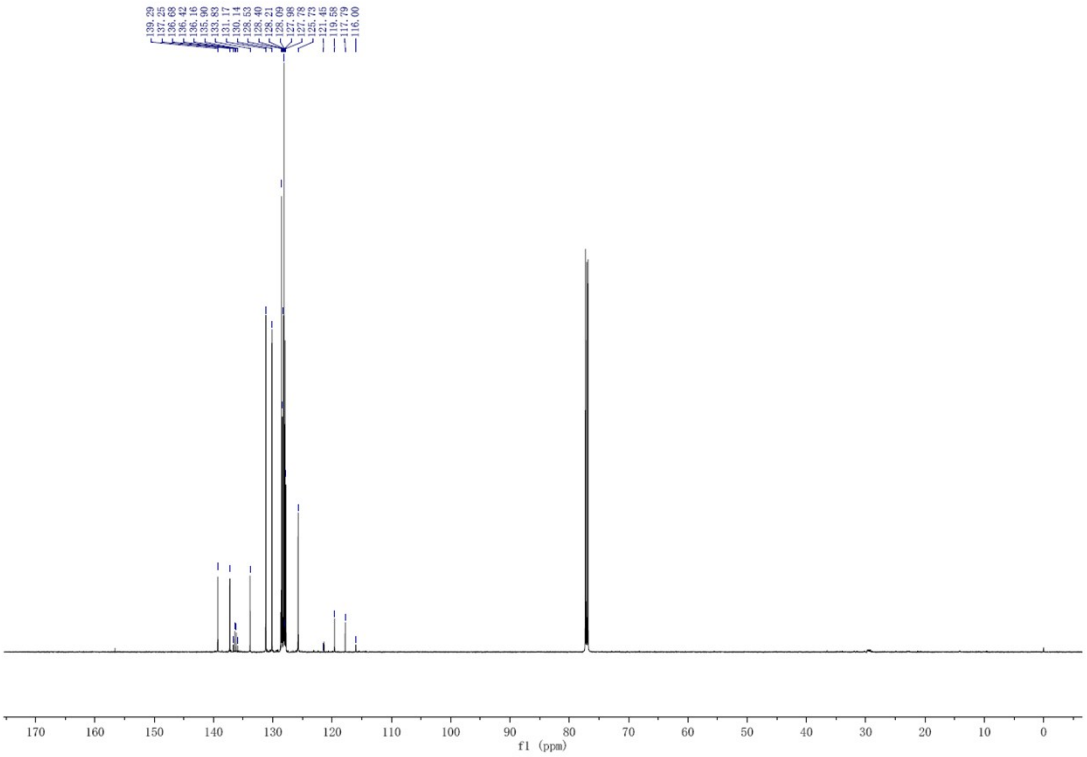
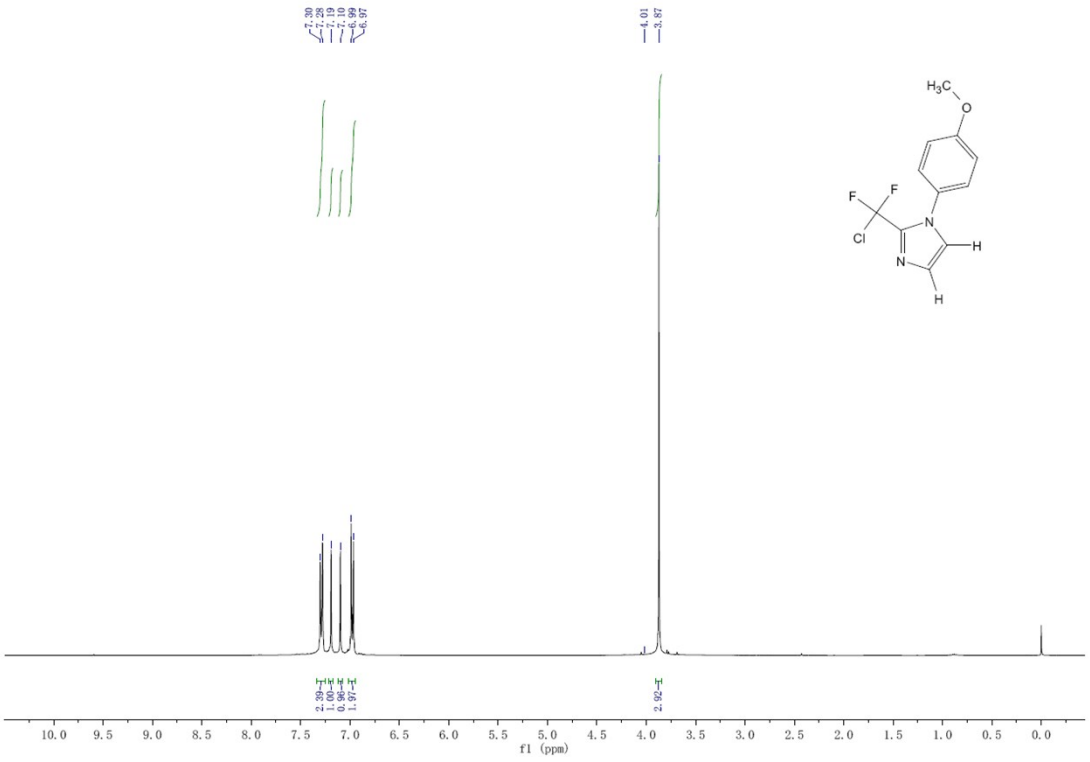
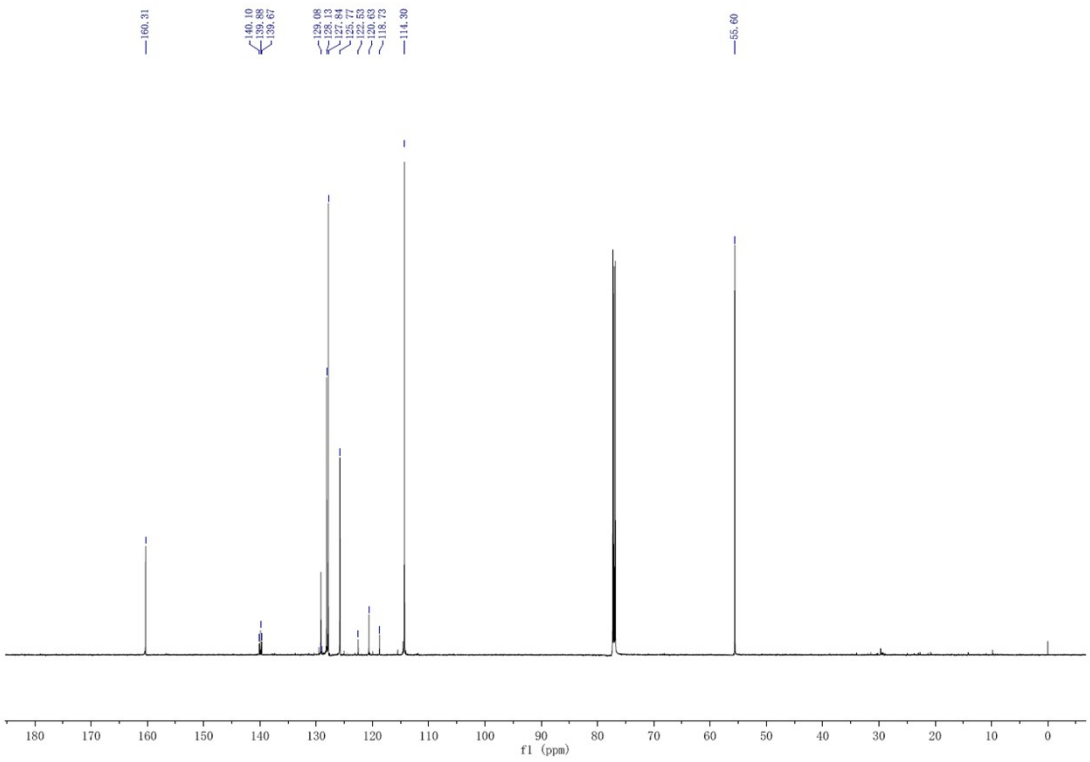
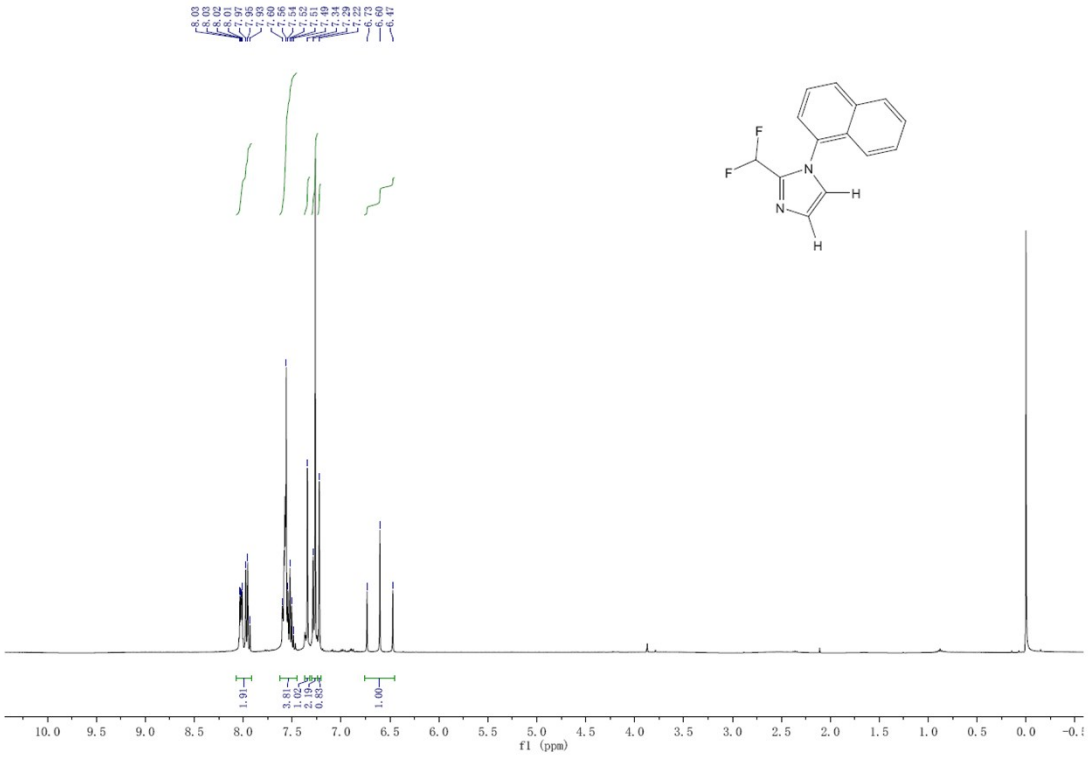
119.69
117.81
116.02
111.89
55.73
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

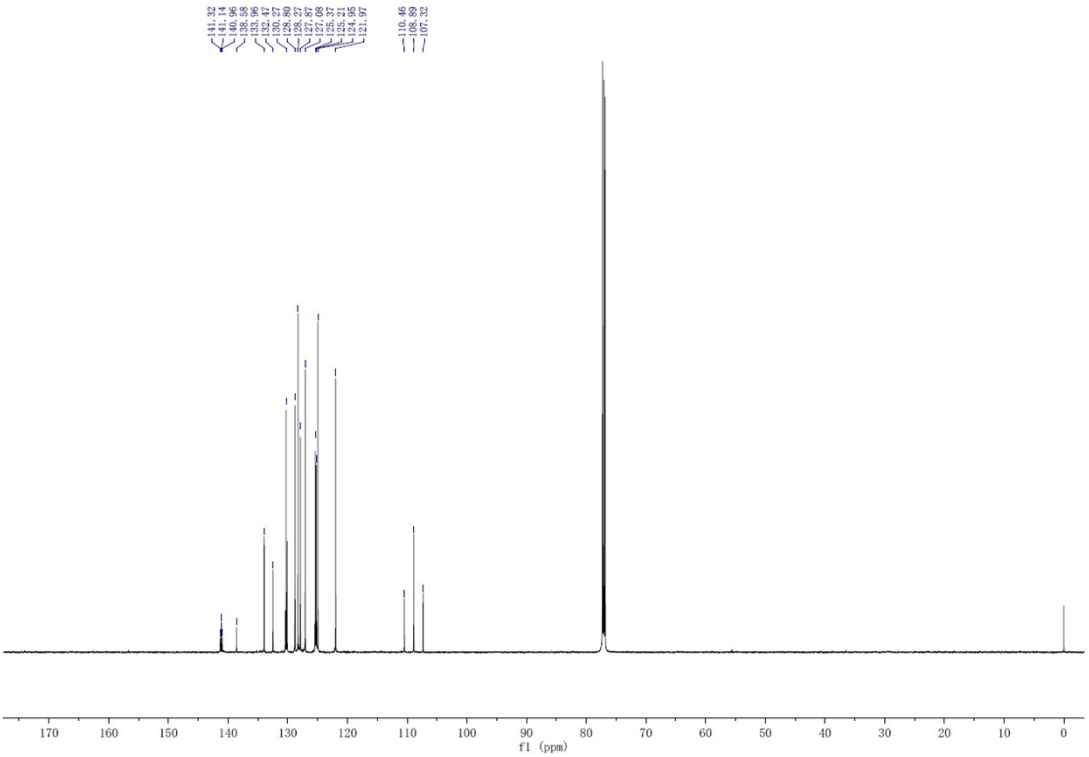

F
F
F
N
N
H
H
f1 (ppm)

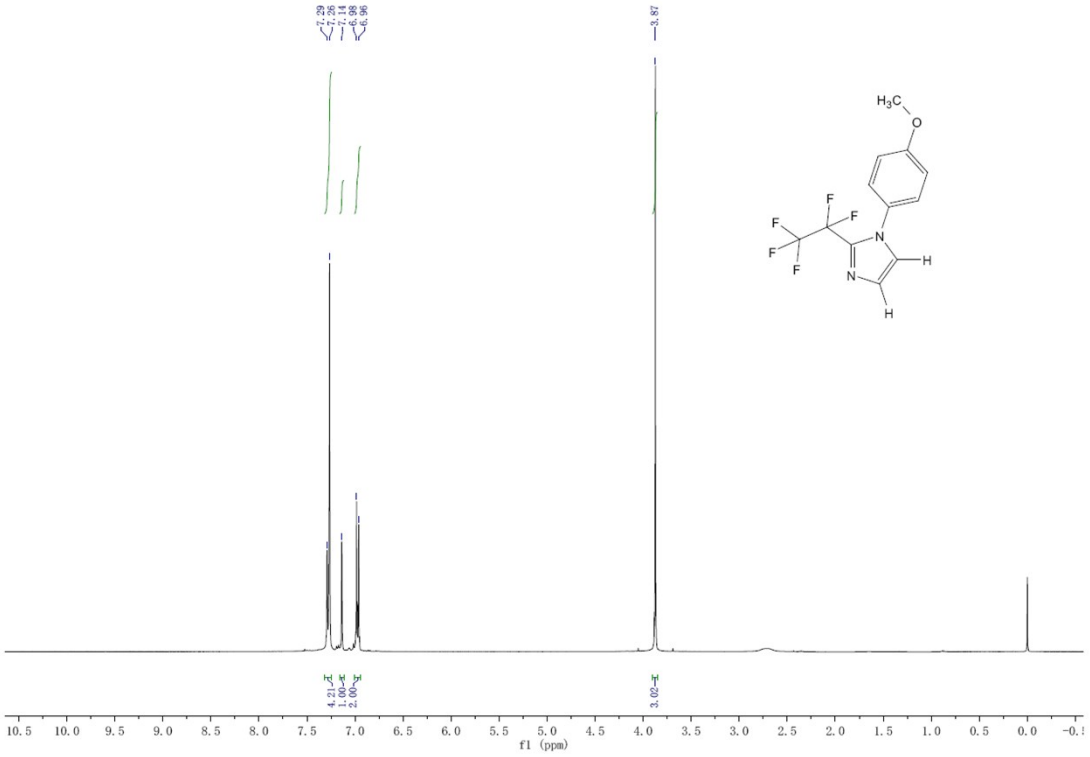

f1 (ppm)

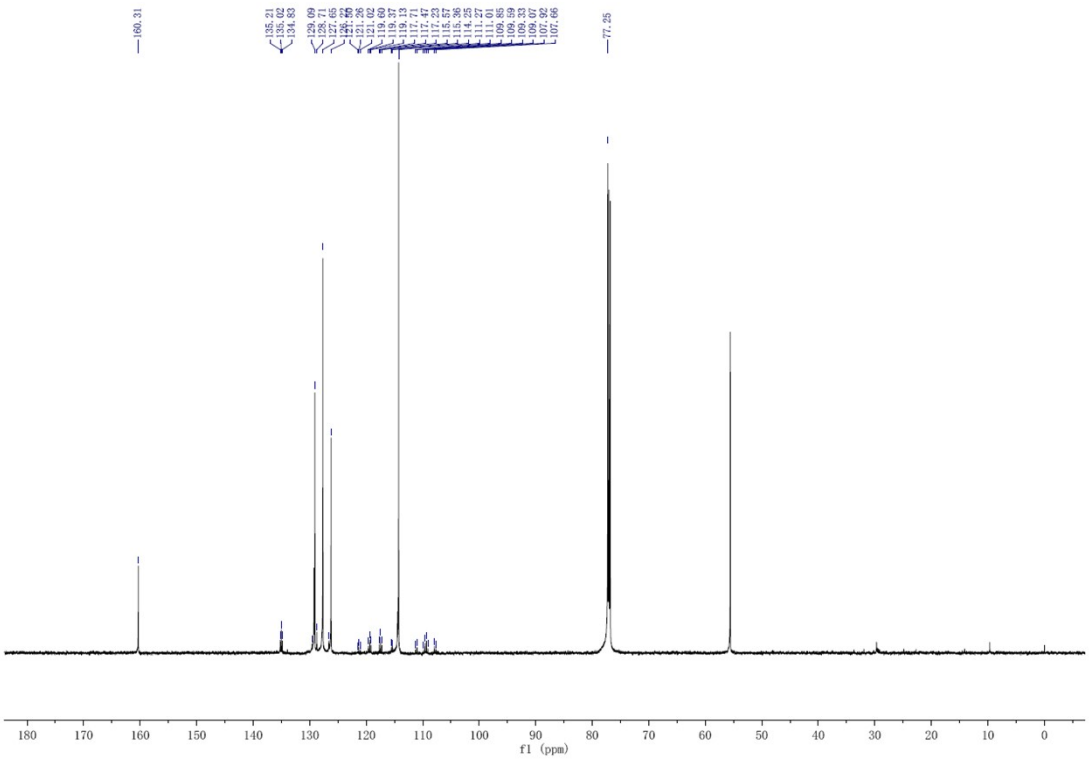

7.30
7.28
7.19
7.10
6.99
6.97
4.01
3.87
2.39
1.00
0.96
1.97
2.92
H3C
O
F
F
Cl
N
N
H
H
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.31
140.10
139.88
139.67
129.08
128.13
127.84
125.77
122.53
120.63
118.73
114.30
55.60
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.03
8.03
8.02
8.01
7.97
7.95
7.93
7.60
7.56
7.54
7.52
7.51
7.49
7.34
7.29
7.22
6.73
6.69
6.47
F
F
N
H
N
H
1.91
3.81
1.02
1.95
0.83
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


141.32
141.14
140.96
138.58
133.96
132.47
130.27
128.89
128.27
127.57
127.08
125.37
125.21
124.95
121.97
110.46
108.89
107.32
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.29
7.26
7.14
6.98
6.96
3.87
H3C
O
F
F
F
F
F
N
N
H
H
4.21
1.00
2.00
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.31
135.21
135.02
134.83
129.09
128.71
127.65
121.26
121.02
119.37
119.13
117.71
115.57
115.36
114.25
111.27
111.01
109.85
109.59
109.33
108.07
107.92
107.66
77.25
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)